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L4: Entry 5 of 256

File: USPT

Jun 28, 2005

DOCUMENT-IDENTIFIER: US 6911572 B1

TITLE: Water-absorbing polymers having supramolecular hollow molecules, method for producing them and use of the same

Abstract Text (1):

The invention relates to absorbent polymers based on optionally partially neutralised, monoethylenically unsaturated, acid group-carrying monomers. The surfaces of said polymers are re-cross-linked. The inventive polymers also have cyclodextrines and/or cyclodextrine derivatives which are covalently and/or ionically bonded and/or included therein.

Brief Summary Text (2):

Commercially available superabsorbing polymers essentially are crosslinked polyacrylic acids, crosslinked starch/acrylic acid graft copolymers, crosslinked hydrolyzed starch/acrylonitrile graft copolymers, crosslinked poly-(maleic anhydride-co-isobutylene), or mixtures of various of the above-mentioned crosslinked polymers, wherein the carboxylic groups have been subjected to partial neutralization with sodium and/or potassium ions.

Brief Summary Text (4):

Such crosslinked polymer products based on monomers containing acid groups are obtained by using one or more primary crosslinkers and one or more secondary crosslinkers and exhibit a combination of properties, namely, high retention, high absorption under pressure, low solubles, and rapid absorption of liquid, which has not been achieved so far. When used in hygiene articles, these crosslinked polymer products have the advantage that secreted fluids, once absorbed by the polymer product, can no longer contact the skin. Thus, skin lesions such as diaper dermatitis can largely be avoided. Such comfort can even be increased by absorbing malodorous compounds.

Brief Summary Text (5):

According to Rompp Chemie Lexikon, the content of urine components is subject to physiological fluctuations; also, particular substances are secreted at concentrations varying within a daily period, so that more precise data on the urine composition invariably are related to the so-called 24 hour urine which, in a healthy adult, contains e.g. urea (average 20 g), uric acid (0.5 g), creatinine (1.2 g), ammonia (0.5 g), amino acids (2 g), proteins (60 mg), reducing substances (0.5 g, about 70 mg of which are D-glucose or urine sugar), citric acid (0.5 g) and other organic acids, as well as certain vitamins (C, B_{sub}.12 etc.). The following inorganic ions are present: Na⁺ (5.9 g), K⁺ (2.7 g), NH₄⁺ (0.8 g), Ca²⁺ (0.5 g), Mg²⁺ (0.4 g); Cl⁻ (8.9 g); PO₄³⁻ (4.1 g), SO₄²⁻ (2.4 g). The dry content is between 50 and 72 g. Inter alia, alkylfurans, ketones, lactones, pyrrole, allyl isothiocyanate, and dimethyl sulfone have been recognized as volatile components of urine. Most of the volatile components are molecules having a molar mass below about 1000 g/mol and a high vapor pressure.

Brief Summary Text (18):

According to the invention, said object is accomplished by providing polymers based on crosslinked monomers bearing optionally partially neutralized acid groups, which

polymers have cyclodextrins and/or derivatives thereof bound ionically and/or covalently and/or incorporated therein.

Brief Summary Text (19):

As a result of the inventive binding to the preferably powdered polymer, the cyclodextrin component can be extracted by the liquid to be absorbed to only a lesser extent, or, in the dry state, undergoes demixing to only a lesser extent. Despite the intimate linkage with the crosslinked absorber bearing acid groups, the polymer according to the invention surprisingly shows excellent absorption of odors which is even enhanced compared to unbound cyclodextrin. In particular, the absorbent polymers exhibit high absorption of odors even in those cases where the cyclodextrin is fixed inside the absorber. This can be established by an effective reduction in the gas concentration of malodorous substances.

Brief Summary Text (24):

Above all, those derivatives are possible which permit chemical linkage by ionic or covalent binding to the monomer bearing acid groups or to the corresponding polymer. Covalent linkages preferably are via C--C bonds as, for example, with cyclodextrin derivatives having ethylenically unsaturated groups incorporated covalently in the polymer chain already during polymerization of the monomers. For example, such groups are (meth)acrylic, (meth)allyl and vinyl groups. According to the invention, however, covalent linkage of the cyclodextrin component to the polymer of ethylenically unsaturated monomers is also possible subsequent to polymerization via ether, amide or ester groups.

Brief Summary Text (26):

Ionic cyclodextrins can be produced by reacting cyclodextrin derivatives with reactive compounds such as chloroacetic acid, sodium chloroacetate, maleic acid, maleic anhydride, and succinic anhydride. In an aqueous solution, these reaction products, e.g. carboxymethylcyclodextrin, carry a negative charge in a basic medium due to the carboxylate group.

Brief Summary Text (41):

Preferably, aliphatic, optionally substituted C.sub.2 -C.sub.10, preferably C.sub.2 -C.sub.5 carboxylic acids or sulfonic acids, such as acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, itaconic acid, vinylacetic acid, vinylsulfonic acid, methallylsulfonic acid, 2-acryl-amido-2-methyl-1-propanesulfonic acid, as well as the alkali and/or ammonium salts or mixtures thereof are possible as ethylenically unsaturated monomers containing acid groups. It is preferred to use acrylic acid and its alkali and/or ammonium salts and mixtures thereof. Furthermore, it is also possible to use monomers being hydrolyzed to form acid groups as late as subsequent to the polymerization, e.g. the corresponding nitrile compounds.

Brief Summary Text (42):

In order to modify the polymer properties, up to 40 wt.-% of monomers other than the monomers containing acid groups, which are soluble in the aqueous polymerization batch, such as acrylamide, methacrylamide, acrylonitrile, (meth)allyl alcohol ethoxylates, and mono(meth)acrylic acid esters of polyhydric alcohols or ethoxylates can optionally be used.

Brief Summary Text (43):

Minor amounts of crosslinking monomers having more than one reactive group in their molecules are copolymerized together with the above-mentioned monomers, thereby forming partially crosslinked polymer products which are no longer soluble in water but merely swellable. Bi- or multifunctional monomers, e.g. methylenebisacryl- or -methacrylamide, or ethylenebisacrylamide may be mentioned as crosslinking monomers, and also, allyl compounds such as allyl (meth)acrylate, alkoxyLATED allyl (meth)acrylate reacted preferably with from 1 to 30 mol of ethylene oxide units, triallyl cyanurate, maleic acid diallyl ester, polyallyl esters, tetraallyloxyethane,

triallylamine, tetraallylethylenediamine, allyl esters of phosphoric acid or phosphorous acid, and also, the N-methylol compounds of unsaturated amides such as methacrylamide or acrylamide and the ethers derived therefrom, as well as esters of polyols and alkoxylated polyols with unsaturated acids, such as diacrylates or triacrylates, e.g. butanediol or ethylene glycol diacrylate, polyglycol di(meth) acrylates, trimethylolpropane triacrylate, di- and triacrylate esters of trimethylolpropane preferably oxyalkylated (ethoxylated) with 1 to 30 mol alkylene oxide, acrylate and methacrylate esters of glycerol and pentaerythritol, and of glycerol and pentaerythritol preferably oxyethylated with 1 to 30 mol ethylene oxide. It is preferred to use triallylamine, acrylates of polyhydric alcohols or alkoxylates thereof, and methallyl alcohol acrylates or alkoxylates thereof. The ratio of crosslinking monomers is from 0.01 to 3.0 wt.-%, preferably from 0.05 to 2.0 wt.-%, and more preferably from 0.05 to 1.5 wt.-%, relative to the total weight of the monomers.

Brief Summary Text (44):

The optional neutralization of the acidic monomers according to the polymerization process of the invention can be performed in various ways. On the one hand, according to the teaching of U.S. Pat. No. 4,654,039, the polymerization may be conducted directly with the acidic monomers, with neutralization being effected subsequently in the polymer gel. Preferably, the acid groups of the monomers are already neutralized to 20-95%, preferably 50-80% prior to polymerization, in which case they are present as sodium and/or potassium and/or ammonium salts at the time polymerization is begun. It is preferred to use those bases for neutralization which do not adversely affect the subsequent polymerization. It is preferred to use sodium or potassium hydroxide solution and/or ammonia, with sodium hydroxide solution being particularly preferred; addition of sodium carbonate, potassium carbonate or sodium bicarbonate may have an additional positive effect as taught in U.S. Pat. Nos. 5,314,420 and 5,154,713. Before initiating the polymerization in this adiabatic solution polymerization, the partially neutralized monomer solution is cooled to a temperature of below 30.degree. C., preferably below 20.degree. C. The other polymerization processes comply with the temperatures known from prior art as apparent from the literature below.

Brief Summary Text (45):

The polymer products of the invention may optionally contain water-soluble natural or synthetic polymers as a basis for grafting in amounts up to 30 wt.-%. Inter alia, these include partially or completely saponified polyvinyl alcohols, starch or starch derivatives, cellulose or cellulose derivatives, polyacrylic acids, polyglycols, or mixtures thereof. The molecular weights of the polymers added as basis for grafting must be adapted to the circumstances of the polymerization conditions. In the event of an aqueous solution polymerization, for example, it may be necessary for viscosity reasons to employ low to medium molecular weight polymers, whereas this factor plays a minor role in a suspension polymerization.

Brief Summary Text (46):

In addition to polymers obtained by crosslinking polymerization of partially neutralized acrylic acid, those are preferably used which are obtained by employing starch or polyvinyl alcohol as graft basis.

Brief Summary Text (47):

The polymerization process of the invention can be initiated by various conditions, e.g. by irradiating with radioactive, electromagnetic or ultraviolet radiation, or by a redox reaction of two compounds, e.g. sodium hydrogen sulfite with potassium persulfate, or ascorbic acid with hydrogen peroxide. The thermally induced decomposition of a so-called free-radical initiator such as azobisisobutyronitrile, sodium peroxodisulfate, t-butyl hydroperoxide, or dibenzoyl peroxide is suitable as well. Furthermore, a combination of some of the above-mentioned polymerization initiators is possible.

Brief Summary Text (49):

According to the first method, the partially neutralized acrylic acid is converted to a gel by means of free-radical polymerization in aqueous solution and in the presence of crosslinkers and optional polymer additives, which gel is subsequently crushed and dried until a powdered, flowable state is reached, milled, and screened to the desired particle size. The solution polymerization may be conducted in a continuous or batchwise fashion. The patent literature includes a broad spectrum of possible variations with respect to concentration conditions, temperatures, type and amount of initiators, as well as a variety of secondary crosslinking options. Typical processes have been described in the following patent specifications: U.S. Pat. Nos. 4,076,663; 4,286,082; DE 27 06 135, DE 35 03 458, DE 35 44 770, DE 40 20 780, DE 42 44 548, DE 43 23 001, DE 43 33 056, DE 44 18 818, the disclosure of which is hereby incorporated by reference.

Brief Summary Text (50):

The inverse suspension and emulsion polymerization process may also be used to produce the polymer products of the invention. According to this process variant, an aqueous, partially neutralized solution of acrylic acid is dispersed in a hydrophobic organic solvent using protective colloids and/or emulsifiers, and the polymerization is initiated using free-radical initiators. The crosslinkers are either dissolved in the monomer solution and pre-charged together with same or added separately and optionally during polymerization. The optionally present polymeric grafting bases are added via the monomer solution or by directly placing in the oil phase. Subsequently, the water is removed azeotropically from the mixture, and the polymer product is filtrated and optionally dried.

Brief Summary Text (51):

Using the process of subsequent surface crosslinking, the polymer products according to the invention are improved in their pattern of properties, particularly in their absorption of liquid under pressure, so that the well-known phenomenon of "gel blocking" is suppressed, where slightly swollen polymer particles adhere to each other, thereby impeding further absorption of liquid and distribution of liquid in the absorbent articles. In this secondary crosslinking, the carboxyl groups of the polymer molecules are crosslinked at the surface of the polymer particles at elevated temperature using crosslinking agents. *Inter alia*, methods of secondary crosslinking have been described in the following publications: DE 40 20 780, EP 317,106 and WO 94/9043. According to the invention, all those surface crosslinking agents known to a person skilled in the art from U.S. Pat. No. 5,314,420, page 8, lines 3-45, may be employed advantageously in combination with a crosslinker used during polymerization or a combination of crosslinkers. As a rule, these compounds contain at least two functional groups capable of reacting with carboxylic acid or carboxyl groups. Alcohol, amine, aldehyde, and carbonate groups are preferred and also, crosslinker molecules having multiple different functions are employed. Preferably, polyols, polyamines, polyaminoalcohols, and alkylene carbonates are used. Preferably, one of the following crosslinking agents is used: ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, glycerol, polyglycerol, propylene glycol, diethanolamine, triethanolamine, polypropylene glycol, block copolymers of ethylene oxide and propylene oxide, sorbitan fatty acid esters, ethoxylated sorbitan fatty acid esters, trimethylolpropane, ethoxylated trimethylolpropane, pentaerythritol, ethoxylated pentaerythritol, polyvinyl alcohol, sorbitol, ethylene carbonate, propylene carbonate. It is particularly preferred to use polyols and ethylene carbonate as surface crosslinking agents. The crosslinking agent is employed in an amount of from 0.0.1 to 30 wt.-%, preferably 0.1-10 wt.-%, relative to the polymer to be crosslinked.

Brief Summary Text (52):

Following polymerization, the polymer product is dried, milled, screened for the respective grain fraction favorable in application-technical terms, and subsequently subjected to surface crosslinking. In some cases, however, it has

proven beneficial to add the surface secondary crosslinkers at an early stage prior to drying the polymer gel or prior to crushing the partially or predominantly dried-polymer. Secondary crosslinking to be performed according to the invention has been described in U.S. Pat. No. 4,666,983 and DE 40 20 780 which hereby are incorporated by reference. Advantageously, the secondary crosslinker frequently is added in the form of a solution in water, organic solvents or mixtures thereof, particularly in those cases where low amounts of secondary crosslinking agent are used. Suitable mixing apparatus for applying the secondary crosslinking agent are, e.g., Patterson-Kelley mixers, DRAIS turbulence mixers, Lodige mixers, Ruberg mixers, screw mixers, pan mixers, and fluid-bed mixers, as well as continuously operated vertical mixers wherein the powder is mixed at a rapid frequency using rotating knives (Schugi mixer). Once the surface crosslinker has been mixed with the crosslinked polymer, heating to temperatures of from 60 to 250.degree. C., preferably from 135 to 200.degree. C., and more preferably from 150 to 185.degree. C. is effected in order to perform the surface crosslinking reaction. The time period of the heat treatment is limited by the risk of destroying the desired pattern of properties of the superabsorbent polymer product as a result of heat damage.

Brief Summary Text (53):

Depending on the type of use, various screening fractions are employed for processing the polymer products as superabsorbers, e.g. between 100 and 1000 .mu.m and preferably between 150 and 850 .mu.m for diapers. In general, this grain fraction is produced by milling and screening prior to and/or subsequent to secondary crosslinking.

Brief Summary Text (59):

The cyclodextrin component may also be added onto the crushed and dried absorbent material during surface crosslinking of the polymer product. Suitable mixing apparatus for applying the crosslinking agent and the cyclodextrin component are e.g. Patterson-Kelley mixers, DRAIS turbulence mixers, Lodige mixers, Ruberg mixers, screw mixers, pan mixers, and fluid-bed mixers, as well as continuously operated vertical mixers wherein the powder is mixed at a rapid frequency using rotating knives (Schugi mixer).

Brief Summary Text (61):

According to the process of the invention, the cyclodextrin component may also be introduced at various stages of the production process, so as to optionally optimize its effect. In this way it is possible, for example, to polymerize a non-modified cyclodextrin together with the monomer solution and fix an ionically modified cyclodextrin on the surface of the polymer during surface crosslinking.

Brief Summary Text (62):

It is also possible to bind the cyclodextrin component to the polymer in an additional surface crosslinking.

Detailed Description Text (8):

Example 1 A) An aqueous solution of acrylic acid (29.3 wt.-%) is mixed with 1.2 wt.-%/monomer of a polyglycol acrylate crosslinker mixture and partially neutralized to 60 mole-% using a 50% sodium hydroxide solution with stirring and cooling. The solution is cooled to 7-8.degree. C. and purged with nitrogen for about 20 minutes. Following addition of aqueous solutions of sodium persulfate, hydrogen peroxide and a water-soluble azo initiator, the polymerization is initiated with ascorbic acid, whereupon a significant rise in temperature to more than 90.degree. C. occurs. A gel-like product is obtained. B) 50 g of the dried and milled polymer from A) screened to 150-800 .mu.m is wetted with a solution of 0.5 g of ethylene carbonate, 2 g of water and 4 g of acetone in a plastic vessel with vigorous stirring and mixed thoroughly using a commercially available household hand mixer (Krups company). Subsequently, the wetted polymer is heated in an oven at a temperature of 180.degree. C. for 30 minutes, thereby undergoing surface

crosslinking. C) The procedure is as described in A). In addition, however, 5 g of cyclodextrin is added to the monomer solution. A gel-like product is obtained, the further processing of which is effected as described in B). D) The gel free of cyclodextrin, which has been obtained in A), is immersed in a:80.degree. C. hot solution in a beaker, consisting of 10 g of cyclodextrin and 23.3 g of water, until the solution has completely permeated into the polymer gel. Subsequently, the gel is willowed and dried at 150.degree. C.

Detailed Description Text (10):

The extractable percentage, EA=8%, determined according to the specified test method, is clearly lower as a result of surface crosslinking.

Detailed Description Text (12):

50 g of the willowed, dried and milled polymer from Example 1 A) screened to 150-800 .mu.m is wetted with a solution of 0.5 g of ethylene carbonate, 1.5 g of non-modified cyclodextrin, and 8.5 g of water in a plastic vessel with vigorous stirring and mixed thoroughly using a commercially available household hand mixer (Krups company). For surface crosslinking, the wetted polymer subsequently is heated in an oven at a temperature of 175.degree. C. for 25 minutes.

Detailed Description Text (14):

Example 3 F) In a 500 ml three-necked round bottom flask, 113.4 g of .beta.-cyclodextrin is suspended in 200 g of deionized water and 8 g of an aqueous sodium hydroxide solution (50%). This suspension is heated to boiling until all of the above is dissolved. With vigorous stirring, 34.4 g of an aqueous solution of DIMAPA-quat. (60%) is added dropwise over 30 min, and this is stirred under reflux for another 5 hours. The solution is cooled to 5.degree. C., and a pH of 7 is adjusted using hydrochloric acid. The precipitate is filtrated and washed with water. Following drying of the filter residue, the DS value is determined to be 0.005 using elemental analysis. 50 g of the willowed, dried and milled polymer from Example 1 B) screened to 150-800 mm is wetted with a solution of 0.5 g of ethylene carbonate, 1.5 g of cyclodextrin derivative according to F), and 7.3 g of water in a plastic vessel with vigorous stirring and mixed thoroughly using a commercially available household hand mixer (Krups company). For surface crosslinking, the wetted polymer subsequently is heated in an oven at a temperature of 175.degree. C. for 25 minutes.

Detailed Description Text (17):

Superabsorbers made of polyacrylic acid with a degree of neutralization of 60% and 70%, respectively, and subjected to secondary surface crosslinking were modified in a second. secondary surface crosslinking according to the procedure of Example 3, using various cyclodextrins. The amount of cyclodextrin can be inferred from the following Table. In the measurement of malodorous substances, a polymer with no cyclodextrin was tested as a blank: according to the specified test procedure, and the gas concentration of malodorous substance found was set 100%. Samples containing cyclodextrin were subsequently tested and the gas concentration of malodorous substance determined.

Detailed Description Paragraph Table (1):

Reduction of ethylfuran concentration Wt.-% CD Cyclodextrin derivative in the gaseous space 10# .beta.-Cyclodextrin 72% 3# .beta.-Cyclodextrin 63% 3# .alpha.-Cyclodextrin 68% #: Absorber having 60% neutralization of the acid groups

Detailed Description Paragraph Table (2):

Reduction of furfurylmercaptane Cyclodextrin or concentration in Wt.-% CD CD derivative the gaseous space 10# .beta.-Cyclodextrin 42% 3# .beta.-Cyclodextrin 51% 3# .alpha.-Cyclodextrin 65% 10# .beta.-Cyclodextrin 46% 3# .beta.-Cyclodextrin 18% 3# .alpha.-Cyclodextrin 28% 1.5# Monochlorotriazinyl-.beta.-cyclodextrin 42% 3# Monochlorotriazinyl-.beta.-cyclodextrin 49% 100 .beta.-Cyclodextrin 57% 100 .alpha.-Cyclodextrin 64% #: Absorber having 70% neutralization of the acid

groups ##: Absorber having 60% neutralization of the acid groups

CLAIMS:

1. An absorbent polymer based on optionally partially neutralized, monoethylenically unsaturated monomers bearing acid groups, the surface of which polymer has been subjected to secondary crosslinking subsequent to polymerizing, wherein the polymer has cyclodextrins and/or cyclodextrin derivatives bound covalently and/or ionically thereto and/or incorporated therein.
5. The polymer according to claim 1, wherein the polymer is constituted up to 40 wt.-% of monoethylenically unsaturated monomers other than the monomers bearing acid groups.
6. The polymer according to claim 1, wherein the polymer has from 0.05 to 3 wt.-% of a crosslinking monomer incorporated by polymerization.
8. The polymer according to claim 1, wherein the polymer has been subjected to surface crosslinking using from 0.1 to 10 wt.-%, relative to the polymer, of a crosslinker component.
13. A process for producing the polymers according to claim 1 by free-radical polymerization of an aqueous solution of the ethylenically unsaturated, optionally partially neutralized monomer bearing acid groups, optionally up to 40 wt.-% of further monoethylenically unsaturated comonomers, crosslinking monomers, and optionally up to 30 wt.-% of a water-soluble natural or synthetic polymer, optional isolation, crushing, and drying of the polymer, wherein the cyclodextrin and/or cyclodextrin derivative is already contained in the polymer during secondary surface crosslinking of same, or the polymer having undergone surface crosslinking is treated with an ionic cyclodextrin derivative.
14. The process according to claim 13, wherein the cyclodextrin and/or cyclodextrin derivative is incorporated prior to or during polymerization of the monomers and/or applied on an optionally obtained hydrogel and/or on optionally milled and dried polymer prior to or during surface crosslinking of the polymer.
23. An absorbent polymer composition comprising a polymer having polymerized units of one or more monoethylenically unsaturated monomers having one or more acid groups, and one or more cyclodextrins, cyclodextrin derivatives, or both, wherein the polymer is secondary surface crosslinked and wherein the cyclodextrins and the cyclodextrin derivatives are at least covalently bonded to the polymer, ionically bonded to the polymer or mixed with the polymer.
31. The composition of claim 23, wherein the polymer comprises up to 40 wt. % of polymerized units of one or more monoethylenically unsaturated monomers other than the monoethylenically unsaturated monomers having acid groups.
32. The composition of claim 23, wherein the polymer further comprises from 0.05 to 3 wt. % of one or more crosslinking monomers bonded to the polymer.
39. A process for producing the composition of claim 23, comprising free-radical polymerization of an aqueous solution comprising one or more ethylenically unsaturated monomers having acid groups, up to 40 wt. % of other monoethylenically unsaturated comonomers, and one or more crosslinking monomers to form a polymer, isolating and drying the polymer, then crosslinking the surface of the polymer to form a surface crosslinked polymer, wherein one or more cyclodextrins, cyclodextrin derivatives, or both are (1) added to the aqueous solution prior to or during the free radical polymerization; (2) applied onto a hydrogel of the polymer; (3) applied to or on the dried polymer; (4) applied to or on the surface crosslinked, dried polymer; or (5) applied to or on the surface of the dried polymer during

crosslinking.

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File: USPT

Feb 1, 2005

DOCUMENT-IDENTIFIER: US 6849665 B2

TITLE: Absorbent compositions

Brief Summary Text (26):

Suitable grafting bases can be of natural or synthetic origin. Examples are starch, cellulose or cellulose derivatives and also other polysaccharides and oligosaccharides, polyvinyl alcohol, polyalkylene oxides, especially polyethylene oxides and polypropylene oxides, polyamines, polyamides and also hydrophilic polyesters. Suitable polyalkylene oxides have for example the formula ##STR1##

Brief Summary Text (28):

Preferred hydrogel-forming polymers are crosslinked polymers having acid groups which are predominantly in the form of their salts, generally alkali metal or ammonium salts. Such polymers swell particularly strongly on contact with aqueous fluids to form gels.

Brief Summary Text (29):

Preference is given to polymers which are obtained by crosslinking polymerization or copolymerization of acid-functional monoethylenically unsaturated monomers or salts thereof. It is further possible to (co)polymerize these monomers without crosslinkers and to crosslink subsequently.

Brief Summary Text (30):

Examples of such monomers bearing acid groups are monoethylenically unsaturated C.sub.3 - to C.sub.25 -carboxylic acids or anhydrides such as acrylic acid, methacrylic acid, ethacrylic acid, .alpha.-chloroacrylic acid, crotonic acid, maleic acid, maleic anhydride, itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid and fumaric acid. It is also possible to use monoethylenically unsaturated sulfonic or phosphonic acids, for example vinylsulfonic acid, allylsulfonic acid, sulfoethyl acrylate, sulfoethyl methacrylate, sulfopropyl acrylate, sulfopropyl methacrylate, 2-hydroxy-3-acryloyloxypropylsulfonic acid, 2-hydroxy-3-methacryloyloxypropylsulfonic acid, vinylphosphonic acid, allylphosphonic acid, styrenesulfonic acid and 2-acrylamido-2-methylpropanesulfonic acid. The monomers may be used alone or mixed.

Brief Summary Text (31):

Preferred monomers are acrylic acid, methacrylic acid, vinylsulfonic acid, acrylamidopropanesulfonic acid or mixtures thereof, for example mixtures of acrylic acid and methacrylic acid, mixtures of acrylic acid and acrylamidopropanesulfonic acid or mixtures of acrylic acid and vinylsulfonic acid.

Brief Summary Text (32):

To optimize properties, it can be sensible to use additional monoethylenically unsaturated compounds which do not bear an acid group but are copolymerizable with the monomers bearing acid groups. Such compounds include for example the amides and nitriles of monoethylenically unsaturated carboxylic acids, for example acrylamide, methacrylamide and N-vinylformamide, N-vinylacetamide, N-methyl-N-vinylacetamide, acrylonitrile and methacrylonitrile. Examples of further suitable compounds are vinyl esters of saturated C.sub.1 - to C.sub.4 -carboxylic acids such as vinyl formate, vinyl acetate or vinyl propionate, alkyl vinyl ethers having at least 2

carbon atoms in the alkyl group, for example ethyl vinyl ether or butyl vinyl ether, esters of monoethylenically unsaturated C.sub.3 - to C.sub.6 -carboxylic acids, for example esters of monohydric C.sub.1 - to C.sub.18 -alcohols and acrylic acid, methacrylic acid or maleic acid, monoesters of maleic acid, for example methyl hydrogen maleate, N-vinylactams such as N-vinyl-pyrrolidone or N-vinylcaprolactam, acrylic and methacrylic esters of alkoxylated monohydric saturated alcohols, for example of alcohols having from 10 to 25 carbon atoms which have been reacted with from 2 to 200 mol of ethylene oxide and/or propylene oxide per mole of alcohol, and also monoacrylic esters and monomethacrylic esters of polyethylene glycol or polypropylene glycol, the molar masses (M.sub.n) of the polyalkylene glycols being up to 2 000, for example. Further suitable monomers are styrene and alkyl-substituted styrenes such as ethylstyrene or tert-butylstyrene.

Brief Summary Text (33):

These monomers without acid groups may also be used in mixture with other monomers, for example mixtures of vinyl acetate and 2-hydroxyethyl acrylate in any proportion. These monomers without acid groups are added to the reaction mixture in amounts within the range from 0 to 50% by weight, preferably less than 20% by weight.

Brief Summary Text (34):

Preference is given to crosslinked polymers of monoethylenically unsaturated monomers which bear acid groups and which are optionally converted into their alkali metal or ammonium salts before or after polymerization and of 0-40% by weight, based on their total weight, of monoethylenically unsaturated monomers which do not bear acid groups.

Brief Summary Text (35):

Preference is given to crosslinked polymers of monoethylenically unsaturated C.sub.3 -C.sub.12 -carboxylic acids and/or their alkali metal or ammonium salts. Preference is given in particular to crosslinked polyacrylic acids, 25-100% of whose acid groups are present as alkali metal or ammonium salts.

Brief Summary Text (36):

Possible crosslinkers include compounds containing at least two éthylenically unsaturated double bonds. Examples of compounds of this type are N,N'-methylenebisacrylamide, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates each derived from polyethylene glycols having a molecular weight of from 106 to 8 500, preferably from 400 to 2 000, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, ethylene glycol diacrylate, ethylene glycol dimethacrylate, propylene glycol diacrylate, propylene glycol dimethacrylate, butanediol diacrylate, butanediol dimethacrylate, hexanediol diacrylate, hexanediol dimethacrylate, allyl methacrylate, diacrylates and dimethacrylates of block copolymers of ethylene oxide and propylene oxide, polyhydric alcohols, such as glycerol or pentaerythritol, doubly or more highly esterified with acrylic acid or methacrylic acid, triallylamine, dialkyldiallylammonium halides such as dimethyldiallylammonium chloride and diethyldiallylammonium chloride, tetraallylethylenediamine, divinylbenzene, diallyl phthalate, polyethylene glycol divinyl ethers of polyethylene glycols having a molecular weight of from 106 to 4 000, trimethylolpropane diallyl ether, butanediol divinyl ether, pentaerythritol triallyl ether, reaction products of 1 mol of ethylene glycol diglycidyl ether or polyethylene glycol diglycidyl ether with 2 mol of pentaerythritol triallyl ether or allyl alcohol, and/or divinylethyleneurea. Preference is given to using water-soluble crosslinkers, for example N,N'-methylenebisacrylamide, polyethylene glycol diacrylates and polyethylene glycol dimethacrylates derived from addition products of from 2 to 400 mol of ethylene oxide with 1 mol of a diol or polyol, vinyl ethers of addition products of from 2 to 400 mol of ethylene oxide with 1 mol of a diol or polyol, ethylene glycol diacrylate, ethylene glycol dimethacrylate or triacrylates and trimethacrylates of addition products of from 6 to 20 mol of ethylene oxide with 1 mol of glycerol, pentaerythritol triallyl ether and/or divinylurea.

Brief Summary Text (37):

Possible crosslinkers also include compounds containing at least one polymerizable ethylenically unsaturated group and at least one further functional group. The functional group of these crosslinkers has to be capable of reacting with the functional groups, essentially the acid groups, of the monomers. Suitable functional groups include for example hydroxyl, amino, epoxy and aziridino groups. Useful are for example hydroxyalkyl esters of the abovementioned monoethylenically unsaturated carboxylic acids, e.g., 2-hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate and hydroxybutyl methacrylate, allylpiperidinium bromide, N-vinylimidazoles, for example N-vinylimidazole, 1-vinyl-2-methylimidazole and N-vinylimidazolines such as N-vinylimidazoline, 1-vinyl-2-methylimidazoline, 1-vinyl-2-ethylimidazoline or 1-vinyl-2-propylimidazoline, which can be used in the form of the free bases, in quaternized form or as salt in the polymerization. It is also possible to use dialkylaminoalkyl acrylates and dialkylaminoalkyl methacrylates such as dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate, diethylaminoethyl acrylate and diethylaminoethyl methacrylate. The basic esters are preferably used in quaternized form or as salt. It is also possible to use glycidyl (meth)acrylate, for example.

Brief Summary Text (38):

Useful crosslinkers further include compounds containing at least two functional groups capable of reacting with the functional groups, essentially the acid groups, of the monomers. Suitable functional groups were already mentioned above, i.e., hydroxyl, amino, epoxy, isocyanate, ester, amido and aziridino groups. Examples of such crosslinkers are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, polyglycerol, triethanolamine, propylene glycol, polypropylene glycol, block copolymers of ethylene oxide and propylene oxide, ethanolamine, sorbitan fatty acid esters, ethoxylated sorbitan fatty acid esters, trimethylolpropane, pentaerythritol, 1,3-butanediol, 1,4-butanediol, polyvinyl alcohol, sorbitol, starch, polyglycidyl ethers such as ethylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, glycerol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, polyglycerol polyglycidyl ether, sorbitol polyglycidyl ether, pentaerythritol polyglycidyl ether, propylene glycol diglycidyl ether and polypropylene glycol diglycidyl ether, polyaziridine compounds such as 2,2-bishydroxymethylbutanol tris [3-(1-aziridinyl)propionate], 1,6-hexamethylenedihydreneurea, diphenylmethanebis-4,4'-N,N'-diethylenurea, halo epoxy compounds such as epichlorohydrin and .alpha.-methylepifluorohydrin, polyisocyanates such as 2,4-toluylene diisocyanate and hexamethylene diisocyanate, alkylene carbonates such as 1,3-dioxolan-2-one and 4-methyl-1,3-dioxolan-2-one, also bisoxazolines and oxazolidones, polyamidoamines and also their reaction products with epichlorohydrin, also polyquaternary amines such as condensation products of dimethylamine with epichlorohydrin, homo- and copolymers of diallyldimethylammonium chloride and also homo- and copolymers of dimethylaminoethyl (meth)acrylate which are optionally quaternized with, for example, methyl chloride.

Brief Summary Text (41):

The polymerization is initiated in the generally customary manner, by means of an initiator. But the polymerization may also be initiated by electron beams acting on the polymerizable aqueous mixture. However, the polymerization may also be initiated in the absence of initiators of the abovementioned kind, by the action of high energy radiation in the presence of photoinitiators. Useful polymerization initiators include all compounds which decompose into free radicals under the polymerization conditions, for example peroxides, hydroperoxides, hydrogen peroxides, persulfates, azo compounds and redox catalysts. The use of water-soluble initiators is preferred. In some cases it is advantageous to use mixtures of different polymerization initiators, for example mixtures of hydrogen peroxide and sodium peroxodisulfate or potassium peroxodisulfate. Mixtures of hydrogen peroxide

and sodium peroxodisulfate may be used in any proportion. Examples of suitable organic peroxides are acetylacetone peroxide, methyl ethyl ketone peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, tert-amyl perpivalate, tert-butyl perpivalate, tert-butyl perneohexanoate, tert-butyl perisobutyrate, tert-butyl per-2-ethylhexanoate, tert-butyl perisononanoate, tert-butyl permaleate, tert-butyl perbenzoate, di(2-ethylhexyl) peroxydicarbonate, dicyclohexyl peroxydicarbonate, di(4-tert-butylcyclohexyl) peroxydicarbonate, dimyristyl peroxydicarbonate, diacetyl peroxydicarbonate, allyl peresters, cumyl peroxyneodecanoate, tert-butyl per-3,5,5-trimethylhexanoate, acetylcylohexylsulfonyl peroxide, dilauryl peroxide, dibenzoyl peroxide and tert-amyl perneodecanoate. Particularly suitable polymerization initiators are water-soluble azo initiators, e.g., 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethylene)isobutyramidine dihydrochloride, 2-(carbamoylazo)isobutyronitrile, 2,2'-azobis[2-(2'-imidazolin-2-yl)propane] dihydrochloride and 4,4'-azobis(4-cyanovaleric acid). The polymerization initiators mentioned are used in customary amounts, for example in amounts of from 0.01 to 5%, preferably from 0.05 to 2.0%, by weight, based on the monomers to be polymerized.

Brief Summary Text (42):

Useful initiators also include redox catalysts. In redox catalysts, the oxidizing component is at least one of the above-specified per compounds and the reducing component is for example ascorbic acid, glucose, sorbose, ammonium or alkali metal bisulfite, sulfite, thiosulfate, hyposulfite, pyrosulfite or sulfide, or a metal salt, such as iron(II) ions or sodium hydroxymethylsulfoxylate. The reducing component in the redox catalyst is preferably ascorbic acid or sodium sulfite. Based on the amount of monomers used in the polymerization, from 3.times.10.⁻⁶ to 1 mol % may be used for the reducing component of the redox catalyst system and from 0.001 to 5.0 mol % for the oxidizing component of the redox catalyst, for example.

Brief Summary Text (43):

When the polymerization is initiated using high energy radiation, the initiator used is customarily a photoinitiator. Photoinitiators include for example .alpha.-splitters, H-abstracting systems or else azides. Examples of such initiators are benzophenone derivatives such as Michler's ketone, phenanthrene derivatives, fluorene derivatives, anthraquinone derivatives, thioxanthone derivatives, coumarin derivatives, benzoin ethers and derivatives thereof, azo compounds such as the abovementioned free-radical formers, substituted hexaarylbisimidazoles or acylphosphine oxides. Examples of azides are: 2-(N,N-dimethylamino)ethyl 4-azidocinnamate, 2-(N,N-dimethylamino)ethyl 4-azidonaphthyl ketone, 2-(N,N-dimethylamino)ethyl 4-azidobenzoate, 5-azido-1-naphthyl 2'-(N,N-dimethylamino)ethyl sulfone, N-(4-sulfonylazidophenyl)maleimide, N-acetyl-4-sulfonylazidoaniline, 4-sulfonylazidoaniline, 4-azidoaniline, 4-azidophenacyl bromide, p-azidobenzoic acid, 2,6-bis(p-azidobenzylidene)cyclohexanone and 2,6-bis(p-azidobenzylidene)-4-methylcyclohexanone. Photoinitiators, if used, are customarily used in amounts of from 0.01 to 5% of the weight of the monomers to be polymerized.

Brief Summary Text (44):

The subsequent crosslinking stage comprises polymers which were prepared by polymerization of the abovementioned monoethylenically unsaturated acids and optionally monoethylenically unsaturated comonomers and which have a molecular weight of more than 5 000, preferably more than 50 000, being reacted with compounds having at least two groups which are reactive toward acid groups. This reaction can take place at room temperature or else at elevated temperatures of up to 220.degree. C.

Brief Summary Text (47):

Crosslinkers are added to the acid-functional polymers or salts in amounts of from 0.5 to 25% by weight, preferably from 1 to 15% by weight, based on the amount of polymer used.

Brief Summary Text (54):

To effect surface postcrosslinking, compounds capable of reacting with the functional groups of the polymers by crosslinking are applied to the surface of the hydrogel particles, preferably in the form of an aqueous solution. The aqueous solution may contain water-miscible organic solvents. Suitable solvents are alcohols such as methanol, ethanol, i-propanol or acetone.

Brief Summary Text (55):

Suitable surface postcrosslinkers include for example: di- or polyglycidyl compounds such as diglycidyl phosphonates or ethylene glycol diglycidyl ether, bischlorohydrin ethers of polyalkylene glycols, alkoxyisilyl compounds, polyaziridines, aziridine compounds based on polyethers or substituted hydrocarbons, for example bis-N-aziridinomethane, polyamines or polyamidoamines and their reaction products with epichlorohydrin, polyols such as ethylene glycol, 1,2-propanediol, 1,4-butanediol, glycerol, methyltriglycol, polyethylene glycols having an average molecular weight M_{sub}w of 200-10 000, di- and polyglycerol, pentaerythritol, sorbitol, the ethoxylates of these polyols and their esters with carboxylic acids or carbonic acid such as ethylene carbonate or propylene carbonate, carbonic acid derivatives such as urea, thiourea, guanidine, dicyandiamide, 2-oxazolidinone and its derivatives, bisoxazoline, polyoxazolines, di- and polyisocyanates, di- and poly-N-methylol compounds such as, for example, methylenebis(N-methylolmethacrylamide) or melamine-formaldehyde resins, compounds having two or more blocked isocyanate groups such as, for example, trimethylhexamethylene diisocyanate blocked with 2,2,3,6-tetramethylpiperidin-4-one.

Brief Summary Text (56):

If necessary, acidic catalysts may be added, for example p-toluenesulfonic acid, phosphoric acid, boric acid or ammonium dihydrogenphosphate.

Brief Summary Text (61):

Electrostatic spacers are also generated by applying a crosslinked, cationic sheath, either by means of reagents capable of forming a network with themselves, for example addition products of epichlorohydrin with polyamidoamines, or by applying cationic polymers capable of reacting with an added crosslinker, for example polyamines or polyimines combined with polyepoxides, multifunctional esters, multifunctional acids or multifunctional (meth)acrylates. It is also possible to use any multifunctional amines having primary or secondary amino groups, for example polyethyleneimine, polyallylamine, polylysine, preferably polyvinylamine. Further examples of polyamines are ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenhexamine and polyethylenimines and also polyamines having molar masses of up to 4 000 000 in each case.

Brief Summary Text (80):

Cellulosic fibers may also be chemically stiffened by chemical reaction. For instance, suitable crosslinker substances may be added to effect crosslinking taking place within the fiber. Suitable crosslinker substances are typical substances used for crosslinking monomers including but not limited to C_{sub}2 - C_{sub}8 -dialdehydes, C_{sub}2 -C_{sub}8 -monoaldehydes having acid functionality and in particular C_{sub}2 -C_{sub}9 -polycarboxylic acids. Specific substances from this series are for example glutaraldehyde, glyoxal, glyoxylic acid, formaldehyde and citric acid. These substances react with at least 2 hydroxyl groups within any one cellulose chain or between two adjacent cellulose chains within any one cellulose fiber. The crosslinking causes a stiffening of the fibers, to which greater dimension stability is imparted as a result of this treatment. In addition to their hydrophobic character, these fibers exhibit uniform combinations of stiffening and elasticity. This physical property makes it possible to retain the capillary structure even under simultaneous contact with fluid and compressive forces and to prevent premature collapse.

Brief Summary Text (81):

Chemically crosslinked cellulose fibers are known and described in WO 91/11162, U.S. Pat. No. 3,224,926, U.S. Pat. No. 3,440,135, U.S. Pat. No. 3,932,209, U.S. Pat. No. 4,035,147, U.S. Pat. No. 4,822,453, U.S. Pat. No. 4,888,093, U.S. Pat. No. 4,898,642 and U.S. Pat. No. 5,137,537. The chemical crosslinking imparts stiffening to the fiber material, which is ultimately reflected in improved dimensional stability for the hygiene article as a whole. The individual layers are joined together by methods known to one skilled in the art, for example intermelting by heat treatment, addition of hot-melt adhesives, latex binders, etc.

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L14: Entry 10 of 20

File: USPT

Jul 3, 1990

DOCUMENT-IDENTIFIER: US 4939063 A

TITLE: Light-sensitive material comprising light-sensitive layer provided on support comprising a coating layer containing a resin

Brief Summary Text (22):

In the present specification, the term "hydrocarbon resin" means a synthetic resin substantially composed of hydrocarbon. Preferably, carbon and hydrogen atoms are present to the extent of at least 90% of the chemical composition of the resin. The hydrocarbon resin has an average molecular weight preferably in the range of 300 to 10,000, and more preferably in the range of 1,000 to 5,000.

Brief Summary Text (25):

Other hydrophobic polymers can be contained in the coating layer in addition to the above-mentioned hydrocarbon resin. The polymer can be a homopolymer or a copolymer. The copolymer may partially contain a hydrophilic repeating unit so long as it is hydrophobic as a whole. Examples of the hydrophobic polymers include polyvinylidene chloride, styrene-butadiene copolymer, methyl methacrylate-butadiene copolymer, acrylonitrilebutadiene copolymer, styrene-acrylate copolymer, methyl methacrylate-acrylate copolymer and styrene-methacrylate-acrylate copolymer.

Brief Summary Text (26):

The hydrophobic polymer preferably has a crosslinked structure. The cross-linked structure can be introduced into the hydrophobic polymer when a conventional hardening agent (crosslinking agent) is used together with the hydrophobic polymer in the course of the preparation of the paper support. Examples of the hardening agents include an active vinyl compound (e.g., 1,3-bis(vinylsulfonyl)-2-propanol, methylenebismaleimide), an active halogen compound (e.g., sodium salt of 2,4-dichloro-6-hydroxy-s-triazine, 2,4-dichloro-6-hydroxy-s-triazine, N,N'-bis(2-chloroethylcarbamyl)piperazine), an epoxy compound (e.g., bis(2,3-epoxypropyl) methylpropylammonium p-toluenesulfonate), and a methanesulfonate compound (e.g., 1,2-di(methane-sulfonyloxy)ethane).

Brief Summary Text (27):

A pigment can be added to the coating layer containing the hydrophobic polymer to improve the smoothness of the surface of the coating layer and to facilitate the formation of the coating layer in the course of the preparation. The pigment may be any of pigments employed in a conventional coated paper (coat paper, art paper, baryta paper etc.). Examples of the inorganic pigments include titanium dioxide, barium sulfate, talc, clay, kaolin, calcined kaolin, aluminum hydroxide, amorphous silica, crystalline silica and synthetic alumina silica. Examples of the organic pigments include polystyrene resin, acrylic resin, urea-formaldehyde resin.

Brief Summary Text (37):

An internal size such as a rosin, a paraffin wax, a higher fatty acid, an alkenylsuccinic acid, a fatty acid anhydride and alkylketene dimer can be added to paper stuff.

Brief Summary Text (38):

A filler (e.g., calcium carbonate, talc, clay, kaolin, titanium dioxide, fine particles of urea resin), a paper strengthening agent (e.g., polyacrylamide,

starch, polyvinyl alcohol), a softening agent (e.g., a reaction product of a maleic anhydride copolymer with a polyalkylene polyamine, a quarternary ammonium salt of a higher fatty acid), a fixing agent (e.g., alminium sulfate, polyamide-polyamine-epichlorohydrin), a colored dye and/or a fluorescent dye can be added to the base paper sheet.

Brief Summary Text (43):

A conventional surface size can be coated on the surface of the base paper sheet prior to coating the layer containing a hydrocarbon resin on the base paper sheet. Examples of the surface size include polyvinyl alcohol, starch, polyacrylamide, gelatin, casein, styrene-maleic anhydride copolymer, alkylketene dimer, polyurethane, an epoxidized fatty acid amide.

Brief Summary Text (45):

There is no specific limitation with respect to silver halide contained in the light-sensitive layer. Examples of the silver halides include silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chloroiodide, silver iodobromide, and silver chloroiodobromide in the form of grains.

Brief Summary Text (46):

The halogen composition of individual grains may be homogeneous or heterogeneous. A silver halide grain can have a core/shell structure in which the silver iodide content in the shell is higher than that in the core. There is no specific limitation on the crystal habit of silver halide grains. For example, a tubular grain having an aspect ratio of not less than 3 can be used.

Brief Summary Text (47):

Two or more kinds of silver halide grains which differ in halogen composition, crystal habit, grain size, and/or other features from each other can be used in combination. There is also no specific limitation on grain size distribution of silver halide grains. For example, the silver halide grains having such a grain size distribution that the coefficient of the variation is not more than 20% can be employed.

Brief Summary Text (55):

Examples of compounds having an ethylenic unsaturated group include acrylic acid, salts of acrylic acid, acrylic esters, acrylamides, methacrylic acid, salts of methacrylic acid, methacrylic esters, methacrylamide, maleic anhydride, maleic esters, itaconic esters, styrene, styrene derivatives, vinyl ethers, vinyl esters, N-vinyl heterocyclic compounds, allyl ethers, allyl esters, and compounds carrying a group or groups corresponding to one or more of these compounds.

Brief Summary Text (72):

Examples of the substances which develop to give a color in contact with other components include various compounds capable of developing a color through some reaction between two or more components, such as acid-base reaction, oxidation-reduction reaction, coupling reaction, chelating reaction, and the like. Examples of such color formation systems are described in Hiroyuki Moriga, "Introduction of Chemistry of Speciality Paper" (in Japanese, 1975). pp. 29-58 (pressure-sensitive copying paper), pp. 87-95 (azo-graphy), pp. 118-120 (heat-sensitive color formation by a chemical change) or in MSS. of the seminar promoted by the Society of Kinki Chemical Industry, "The Newest Chemistry of Coloring Matter - Attractive Application and New Development as a Functional Coloring Matter", pp. 26-32 (June 19, 1980).

Brief Summary Text (76):

When the heat development is employed in the use of the light-sensitive material, an organic silver salt is preferably contained in the light-sensitive material. It can be assumed that the organic silver salt takes part in a redox reaction using a silver halide latent image as a catalyst when heated to a temperature of 80.degree.

C. or higher. In such case, the silver halide and the organic silver salt preferably are located in contact with each other or close together. Examples of organic compounds employable for forming such organic silver salt include aliphatic or aromatic carboxylic acids, thiocarbonyl group-containing compounds having a mercapto group or an alpha-hydrogen atom, imino group-containing compounds, and the like. Among them, benzotriazoles are most preferable. The organic silver salt is preferably used in an amount of from 0.01 to 10 mol., and preferably from 0.01 to 1 mol., per 1 mol. of the light-sensitive silver halide. Instead of the organic silver salt, an organic compound (e.g., benzotriazole) which can form an organic silver salt in combination with an inorganic silver salt can be added to the light-sensitive layer to obtain the same effect.

Brief Summary Text (79):

The base precursors preferably are those capable of releasing bases upon reaction by heating, such as salts between bases and organic acids capable of decarboxylation by heating, compounds capable of releasing amines through intramolecular nucleophilic substitution, Lossen rearrangement, or Beckmann rearrangement, and the like; and those capable of releasing bases by electrolysis. Preferred examples of the base precursors include guanidine trichloroacetate, piperidine trichloroacetate, morpholine trichloroacetate, p-toluidine trichloroacetate, 2-picoline trichloroacetate, guanidine phenylsulfonylacetate, guanidine 4-chlorophenylsulfonylacetate, guanidine 4-methylsulfonylphenylsulfonylacetate, and 4-acetylaminomethyl propionate.

Brief Summary Text (96):

The coating solution can be prepared by mixing liquid compositions each containing a component of the light-sensitive layer. Liquid composition containing two or more components may be also used in the preparation of the coating solution. Some components of the light-sensitive layer can be directly added to the coating solution or the liquid composition. Further, a secondary composition can be prepared by emulsifying the oily (or aqueous) composition in an aqueous (or oily) medium to obtain the coating solution.

Brief Summary Text (98):

The silver halide emulsion can be prepared by the acid process, neutral process or ammonia process. In the stage for the preparation, a soluble silver salt and a halogen salt can be reacted in accordance with the single jet process, double jet process or a combination thereof. A reverse mixing method, in which grains are formed in the presence of excess silver ions, or a controlled double jet process, in which a pAg value is maintained constant, can be also employed. The silver halide emulsion may be of a surface latent image type that forms a latent image predominantly on the surface of silver halide grains, or of an inner latent image type that forms a latent image predominantly in the interior of the grains. A direct reversal emulsion comprising an inner latent image type emulsion and a nucleating agent may be used.

Brief Summary Text (99):

In the preparation of the silver halide emulsions, hydrophilic colloids (e.g., gelatin) are advantageously used as protective colloids to improve the sensitivity of the light-sensitive material. In the formation of silver halide grains in the silver halide emulsion, ammonia, an organic thioether derivative or sulfur-containing compound can be used as a silver halide solvent. Further, in the grain formation or physical ripening, a cadmium salt, a zinc salt, a lead salt, a thallium salt, or the like can be introduced into the reaction system. Furthermore, for the purpose of overcoming high or low intensity reciprocity law failure, a water-soluble iridium salt, e.g., iridium (III) or (IV) chloride, or ammonium hexachloroiridate, or a water-soluble rhodium salt, e.g., rhodium chloride can be used.

Brief Summary Text (103):

In preparation of the light-sensitive material, the polymerizable compounds are used as the medium for preparation of the liquid composition containing another component of the light-sensitive layer. For example, the silver halide, including the silver halide emulsion), the reducing agent, or the color image forming substance can be dissolved, emulsified or dispersed in the polymerizable compound to prepare the light-sensitive material. Especially, the color image forming substance is preferably incorporated in the polymerizable compound. Further, the necessary components for preparation of a microcapsule such as shell material can be incorporated into the polymerizable compound.

Brief Summary Text (104):

The light-sensitive composition which is the polymerizable compound containing the silver halide can be prepared using the silver halide emulsion. The light-sensitive composition can be also prepared using silver halide powders which can be prepared by lyophilization. These light-sensitive composition can be obtained by stirring the polymerizable compound and the silver halide using a homogenizer, a blender, a mixer or other conventional stirring device.

Brief Summary Text (105):

Polymers having a principal chain consisting essentially of a hydrocarbon chain substituted in part with hydrophilic groups which contain, in their terminal groups, --OH or nitrogen having a lone electron-pair are preferably introduced into the polymerizable compound prior to the preparation of the light-sensitive composition. The polymer has a function of dispersing silver halide or other component in the polymerizable compound very uniformly as well as a function of keeping thus dispersed state. Further, the polymer has another function of gathering silver halide along the interface between the polymerizable compound (i.e., light-sensitive composition) and the aqueous medium in preparation of the microcapsule. Therefore, using this polymer, silver halide can be easily introduced into the shell material of the microcapsule.

Brief Summary Text (106):

The light-sensitive composition can be also prepared by dispersing microcapsule containing silver halide emulsion as a core structure in the polymerizable compound instead of employing the above polymer.

Brief Summary Text (107):

The polymerizable compound (including the light-sensitive composition) are preferably emulsified in an aqueous medium to prepare the coating solution. The necessary components for preparation of the microcapsule, such as shell material can be incorporated into the emulsion. Further, other components such as the reducing agent can be added to the emulsion.

Brief Summary Text (108):

The emulsion of the polymerizable compound can be processed for forming shell of the microcapsule. It is preferable, though not limitative, that the microcapsule is prepared by emulsifying core materials containing the polymerizable compound and forming a polymeric membrane (i.e., shell) over the core materials.

Brief Summary Text (109):

When the emulsion of the polymerizable compound (including the dispersion of the microcapsule) has been prepared by using the light-sensitive composition, the emulsion can be used as the coating solution of the light-sensitive material. The coating solution can be also prepared by mixing the emulsion of the polymerizable compound and the silver halide emulsion. The other components can be added to the coating solution in a similar manner as the emulsion of the polymerizable compound.

Detailed Description Text (4):

In a disk refiner, 25 weight parts of a laubholz bleached sulfite pulp (LBSP) and

75 weight parts of a laubholz bleached kraft pulp (LBKP) were beaten to obtain a pulp having Canadian standard freeness of 270 cc. To the obtained pulp were added 0.2 weight part of alkylketene dimer, 0.3 weight part of polyamide-polyamineepichlorohydrin, 0.1 weight part of epoxidation fatty acid amide and 0.5 weight part of cationic polyacrylamide to obtain a paper stuff, in which the part was a dry weight ratio to one part of the pulp. A base sheet sheet having basis weight of 70 g/m.² and thickness of 72 .mu.m was prepared from the obtained paper stuff using a Fourdrinier paper machine.

Detailed Description Text (9):

In 1,000 ml of water were dissolved 20 g of gelatin and 3 g of sodium chloride, and the resulting gelatin solution was kept at 75.degree. C. To the gelatin solution, 600 ml of an aqueous solution containing 21 g of sodium chloride and 56 g of potassium bromide and 600 ml of an aqueous solution containing 0.59 mole of silver nitrate were added simultaneously at the same feed rate over a period of 40 minutes to obtain a silver chlorobromide emulsion having cubic grains, uniform grain size distribution, a mean grain size of 0.35 .mu.m and a bromide content of 80 mole %.

Detailed Description Text (12):

In 3,000 ml of water were dissolved 28 g of gelatin and 13.2 g of benzotriazole, and the solution was kept at 40.degree. C. while stirring. To the solution was added 100 ml of an aqueous solution of 17 g of silver nitrate over 2 min. Excessive salts were sedimented and removed from the resulting emulsion by pH-adjustment. Thereafter, the emulsion was adjusted to pH 6.30 to obtain a silver benzotriazole emulsion. The yield of the emulsion was 400 g.

Detailed Description Text (13):

Preparation of Light-Sensitive Composition

Detailed Description Text (16):

To the resulting solution was added a solution in which 0.16 g of the following reducing agent (I) and 1.22 g of the following reducing agent (II) are dissolved in 1.80 g of methylene chloride. ##STR3##

Detailed Description Text (17):

To the resulting solution were added 3.50 g of the silver halide emulsion and 3.35 g of the silver benzotriazole emulsion, and the mixture was stirred at 15,000 r.p.m. for 5 minutes to obtain a light-sensitive composition.

Detailed Description Text (19):

To 10.51 g of 18.6% aqueous solution of Isobam (tradename of Kuraray Co., Ltd.) was added 48.56 g of 2.89% aqueous solution of pectin. After the solution was adjusted to a pH of 4.0 using 10% sulfuric acid, the light-sensitive composition was added to the resulting solution, and the mixture was stirred at 7,000 r.p.m. for 2 minutes to emulsify the light-sensitive composition in the aqueous medium.

Detailed Description Text (20):

To 72.5 g of the aqueous emulsion were added 8.32 g of 40% aqueous solution of urea, 2.82 g of 11.3% aqueous solution of resorcinol, 8.56 g of 37% aqueous solution of formaldehyde and 3.00 g of 8.00% aqueous solution of ammonium sulfate in order, and the mixture was heated at 60.degree. C. for 2 hours while stirring. After the mixture was adjusted to a pH of 7.3 using 10% aqueous solution of sodium hydroxide, 3.62 g of 30.9% aqueous solution of sodium hydrogen sulfite was added to the mixture to obtain a dispersion containing light-sensitive microcapsules.

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<u>L14</u>	L13 and chloride	20	<u>L14</u>
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<u>L12</u>	L6 and sulfate	35	<u>L12</u>
<u>L11</u>	L10 and notrate	0	<u>L11</u>
<u>L10</u>	L6 and sulfate	35	<u>L10</u>
<u>L9</u>	L7 and polyallyl alcohol	0	<u>L9</u>
<u>L8</u>	L7 and polyallyl	1	<u>L8</u>
<u>L7</u>	L6 and polyvinyl same amine	30	<u>L7</u>
<u>L6</u>	l5 and membrane	50	<u>L6</u>
<u>L5</u>	L4 and composition	220	<u>L5</u>
<u>L4</u>	L3 and acid	256	<u>L4</u>
<u>L3</u>	polyamine same polyvinyl alcohol and crosslinking	261	<u>L3</u>
<u>L2</u>	polyamine same polyvinyl alcohol and crosslinking	0	<u>L2</u>
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L25: Entry 12 of 14

File: USPT

Jan 1, 1980

DOCUMENT-IDENTIFIER: US 4181675 A
TITLE: Process for methanol production

Abstract Text (1):

An improved methanol synthesis process is provided wherein synthesis gas containing hydrogen and carbon dioxide is passed over a methanol synthesis catalyst, cooled to condense methanol and water in the reacted gas, the liquids separated, a purge gas stream removed while the remaining reacted gas is recycled to the synthesis catalyst, the purge gas separated by contacting the outer surfaces of a plurality of hollow fiber membranes selectively permeable to hydrogen and carbon dioxide to form a permeant gas depleted in hydrogen and carbon dioxide and a permeate gas enriched in said gases and the enriched permeate gas is combined with the synthesis gas. In an optional embodiment, methanol vapor is first recovered from the purge gas prior to contacting the selectively permeable membranes, preferably by a water scrub.

Brief Summary Text (1):

This invention relates to a process for producing methanol and in particular such process wherein the yield of methanol is improved by the employment of semi-permeable hollow fiber membranes.

Brief Summary Text (6):

We have now found that a methanol synthesis process utilizing semi-permeable hollow fiber membranes for the recovery of significant amounts of the synthesis gas values present in a purge gas stream provides an improved synthesis process with significantly increased yield of methanol product.

Brief Summary Text (7):

According to the invention there is provided a methanol production process in which synthesis gas comprising hydrogen and carbon dioxide is passed over a methanol synthesis catalyst, cooled to condense and remove methanol and water contained in a gas mixture, a portion of uncondensed gases are removed as purge and passed into contact with the outer surfaces of a plurality of semi-permeable hollow fiber membranes selectively permeable to hydrogen and carbon dioxide and the permeated gas concentrated in hydrogen and carbon dioxide is combined with a synthesis gas mixture for contact with the methanol synthesis catalyst. Alternatively, prior to contacting the purge gas stream with the semipermeable hollow fiber membranes such stream is treated to recover any methanol present as vapor. This treatment may take the form of cooling by chilled liquid in heat exchange, refrigeration or the like to condense substantially all of the remaining vaporous methanol. It may also comprise adsorption on a solid adsorbent such as activated carbon or silica, or absorption by an absorbing liquid. Most preferably, such alternative treatment will comprise scrubbing with water as absorbent since the recovery of methanol vapor is essentially complete with a water scrub.

Brief Summary Text (8):

It has been found that substantial advantages are inherent in the process for methanol synthesis wherein the purge gas stream is subjected to permeation through semipermeable hollow fiber membranes selectively permeable to hydrogen and carbon dioxide. The predominant portion of the hydrogen and of the carbon dioxide present

in the purge gas stream are recovered in the form of a permeated gas stream which is suitable for reintroduction to the process thereby increasing the yield of methanol product. Because such permeation provides for recovery of predominant portions of these gases an increased rate of purge is desirable, which assures the removal of sufficient amounts of the inert gases such as methane and nitrogen to balance such withdrawal with new portions charged with the synthesis gas feed and prevents the buildup of such inert gases in the system. Contact of the purge gas stream with the outer surfaces of the preferred large internal diameter hollow fiber membranes discussed below also provides that the permeated gas stream of recovered hydrogen and carbon dioxide gases be at a sufficient pressure relative to the pressure of the purge gas stream that it can be reintroduced into the synthesis process with a minimum amount of additional compression required. The increased purge rates desired for balance of inert gases within the system do not exact any penalty in the form of lost methanol product values if the optimal alternative of scrubbing the purge gas stream with water absorbent prior to its separation over the hollow fiber membranes is employed since the water scrubbing will recover essentially all of the methanol vapor present in the purge stream.

Brief Summary Text (9):

In accordance with the present invention it is preferred that the purge gas stream to be permeated contact the outer surface of hollow fiber membranes having somewhat larger internal and external diameters than those previously preferred by the prior art. In most previous hollow fiber membrane separation devices designed for contacting gas streams the desire for very large membrane active surface areas for contact with such gas streams have led the developers to prescribe very small hollow fibers as membranes with small outside and inside diameters. For example, in U.S.P. 3,339,341, Maxwell et al teach that hollow fibers having outside diameters of between 20 and 250 microns are especially preferred, see Col. 4, lines 65-70 and at Col. 14, line 63 where they record that a semi-commercial installation utilized hollow fibers of 29.2 microns inside diameter. Others have similarly found that hollow fibers having relatively small outside diameters are advantageous for utilization in separation apparatus in order to provide sufficiently large membrane surface areas and other advantages such as capacity to withstand relatively large pressure differentials. For example, Mahon in U.S. Pat. No. 3,228,877 teaches that hollow fibers should have relatively small outside diameters and that the more advantageous range of such outside diameters is between 10 and 50 microns see Col. 11, lines 4-20.

Brief Summary Text (10):

When applied to the separation of gaseous mixtures in practice, though, it has been found that the small inside and outside diameter hollow fiber membranes frequently suffer a severe disadvantage in the extent of pressure drop experienced both along and through such hollow fiber membranes, whereas it is generally desirable that the streams of separated gases be maintained as pressures which are substantial percentages of initial pressure of the gas stream to be separated. Thus, it is generally desired to minimize pressure drop across the membrane separation apparatus, so long as this is consistent with sufficient pressure drop across the semi-permeable membrane itself as to maintain good rates of permeation for permeating gases. For example, in the prior art it has been shown by Gardner et al in Chemical Engineering Progress October 1977, pages 76-78 that large pressure drops are commonly encountered. Thus, in FIG. 4, page 77 in relation to a process using hollow fiber membranes for separating hydrogen and carbon monoxide feed stream that the pressure drop along the length of the very small diameter fiber bores is some 45 percent of the initial 422 kg/cm.² (600 psig) pressure and the pressure drop in the permeated gas stream passing through such membranes amounts to 83.5 percent of the original pressure.

Brief Summary Text (13):

Advantages have been found in the use of hollow fiber membranes when such membranes have relatively large outside diameters and wall thicknesses as described above.

These advantages are best observed when the feed gas mixture is fed radially or axially. By radial feed is meant that the gas mixture is introduced in the mid portion of a bundle of hollow fibers and flows substantially perpendicularly to the orientation of the hollow fibers. By axial feed is meant that the gas mixture is introduced at an outside portion of the fiber bundle, flows generally in the same direction as the orientation of the fibers, and exits at another portion of the fiber bundle. Though often radial feed is considered to provide better gas separation efficiencies, axial feed is frequently more desirable since the separation apparatus may be less complex in design than radially fed separation apparatus. Since no radial feed conduit need be positioned within the bundle, the bundles employed for axial flow may comprise a greater ratio of available membrane surface area for a given volume of separation apparatus than that of a radially fed apparatus. Shell side feed to hollow fiber separation apparatus can provide certain advantages. For instance, a greater surface area for effecting the separation is provided at the exterior surfaces of hollow fibers than at the interior surface of those fibers. Moreover, hollow fibers are generally able to withstand higher pressure differentials when the higher pressures are on the exterior as opposed to the interior of the fibers since generally most materials exhibit greater compressive than tensile strength. In accordance with the present invention it has been found that the improved methanol synthesis process is most advantageously carried out when the separated portion of the uncondensed reaction gases, i.e. the purge gas stream, is contacted with the outside or shell side of the hollow fiber membranes positioned in bundles within separation apparatus vessels arranged for radial or more preferably axial flow, and in which the desired permeate gas stream of concentrated hydrogen and carbon dioxide is withdrawn from the bores of said hollow fiber membranes.

Brief Summary Text (21):

Recovery of the methanol vapor present in the purge gas stream reduces the volume of methanol vapor in the purge gas to very low levels. It thus contributes to the extended life of the hollow fiber membranes subsequently contacted by the purge gas. Some polymer membranes have been found to be sensitive to concentrations of methanol vapor at or near saturation. Desirably, such treatments as a water scrub will reduce the concentration of methanol vapor to less than 20 percent of saturation and preferably to less than 10 percent of saturation in the purge gas stream prior to contact thereof with the fiber membranes.

Brief Summary Text (23):

The purge gas stream, preferably after substantial removal of methanol vapor therefrom is contacted with the semi-permeable hollow fiber membranes for separation into an inert gas and hydrogen stream for a fuel use and a hydrogen and carbon dioxide concentrate for recycle to the methanol synthesis. For contact with the semi-permeable membranes the purge gas stream will be at essentially the pressure of the gas/liquid separator, and in a typical low pressure methanol synthesis process from about 30 to about 100 atmospheres. Preferably the purge gas will be at a pressure of from about 40 to 55 atmospheres and typically at about 44 to 47 atmospheres. The purge gas stream will generally be at a temperature of from about 10.degree. to about 50.degree. C., preferably at from 20.degree. to 45.degree. C. and typically at about 40.degree. C.

Brief Summary Text (24):

The purge gas stream is contacted with a hollow fiber separation membrane which exhibits selectivity to the permeation of hydrogen and carbon dioxide as compared to the permeation of methane and the other inert gases present, if any, such as nitrogen and possibly argon. In view of the generally substantially higher volume concentration of hydrogen in the purge gas stream as compared to that of methane, the separation methane need not exhibit high selectivity for separation of hydrogen from methane in order to provide for an effective purging of the methane and recovery of the hydrogen and carbon dioxide values in such purge stream. Generally, the selectivity for separation of a membrane is described in terms of the ratio of

the permeability of the fast permeating gas, i.e. hydrogen, to the permeability of the slow permeating gas, i.e. methane, wherein the permeability of the gas through the membrane can be defined as a volume of gas, at standard temperature and pressure which passes through the membrane per square centimeter of surface area per second for a partial pressure drop of 1 centimeter of mercury across the membrane per unit thickness. This ratio is referred to as the separation factor of a membrane for the specific gases the permeability of which are used. Desirably, the separation factor of the selected membranes for hydrogen over methane is at least about 10. Separation factors for hydrogen over methane of 80 or 100 or greater may be provided by certain membranes. For the concentration of carbon dioxide in the permeated gas stream the selected membranes should also possess a separation factor for carbon dioxide over methane of from 2 to about 50 and preferably from about 5 to 25. The higher the permeability of hydrogen and carbon dioxide through the selected membrane, the less effective membrane surface area is required to pass the desired amounts of hydrogen and carbon dioxide and substantially reject the methane present in the purge gas stream. Particularly desirable membranes exhibit hydrogen permeabilities of at least 1×10^{-6} , preferably at least 1×10^{-5} to 1×10^{-4} cubic centimeters of hydrogen per square centimeter of membrane surface area per second at a partial pressure drop of 1 centimeter of mercury across the membrane. Likewise, particularly desirable membranes for use in this process also exhibit carbon dioxide permeabilities of at least about 1×10^{-6} and preferably 5×10^{-6} to 5×10^{-5} cu. centimeters of carbon dioxide per square centimeter of membrane surface area per second at a partial pressure drop of 1 centimeter of mercury across the membrane.

Brief Summary Text (25):

The most effective membrane surface area is an area sufficient to permeate as much as possible of the desired hydrogen and carbon dioxide gases present while rejecting to the shell or permeant gas stream desired amounts of the inert gases present in the purge gas stream. Generally this will be an amount of methane sufficient to balance the methane coming into the methanol synthesis process from the stream reforming operation. Factors influencing the determination of the amount of effective membrane surface area include the relative permeation rate of hydrogen and carbon dioxide as well as that of methane through the membrane under the separation conditions including temperature, absolute pressure, and partial pressure differentials of the hydrogen, carbon dioxide and methane gases across the membrane.

Brief Summary Text (26):

Partial pressure differentials of hydrogen and carbon dioxide across the membrane provide the driving force for the permeation of hydrogen and carbon dioxide and depend not only on the total pressure but on the concentration of hydrogen and carbon dioxide on each side of the membrane. Advantageous pressure differentials across the membrane are at least about 3 atmospheres of hydrogen. In many instances hydrogen pressure differentials across the membrane can be considerably greater, from about 5 to about 50 atmospheres and preferably from about 6 to about 30 atmospheres. Sufficient effective membrane surface area and pressure differential is provided that at least about 25 percent and preferably from about 30 to about 80 percent of the hydrogen in the purge gas stream permeates the separation membrane.

Brief Summary Text (27):

In the present invention the separator vessel contains membranes in hollow fiber membrane form with a plurality of the hollow fiber membranes arranged substantially parallel in bundle form. The purge gas stream is contacted on the outside surfaces (shell side) of the hollow fiber membranes and either radial or preferably axial flow along and about the hollow fiber membranes is established. Shell side effluent or permeant gas mixture from the separator can be within 1 to 3 atmospheres of the pressure of the purge gas stream fed to the separator. Hence very little pressure drop is experienced on the shell side of the hollow fiber membranes in either

radial or axial flow. If preferred axial flow is employed the present process is found to be advantageous either in concurrent or countercurrent mode, although it is most preferred to operate in a countercurrent manner. Thus, by establishing countercurrent flow by admitting the purge gas stream at the end of a hollow fiber membrane separator from which the bore effluent product is removed an increased hydrogen partial pressure differential across the hollow fiber membranes is maintained since the concentration of hydrogen increases in the bore as it flows in the direction in which the higher concentration of hydrogen is present in the purge gas stream.

Brief Summary Text (28):

The separator containing the hollow fiber separation membranes may be of any suitable design for gas separations, providing for shell side radial or more preferably axial flow about the hollow fiber membranes. Thus the separator vessel may be either single or double-ended radial flow design wherein the purge gas stream is admitted to a gas feed conduit positioned at the center of the fiber membrane bundle, the permeate gas product is withdrawn from the bores of the hollow fibers at either one or both ends of the vessel, and the permeant gas is removed from either one or both ends of the shell of the separator vessel.

Brief Summary Text (30):

Any suitable material selectively permeable to hydrogen and carbon dioxide in favor of methane and other inert gases may be employed for the hollow fiber separation membrane. Typical membrane materials include organic polymers or organic polymers mixed with inorganics such as fillers, reinforcements, and the like. Metallic and metal-containing membranes may also be employed. Polymers which may be suitable for the separation membranes can be substituted or unsubstituted polymers and may be selected from polysulfones; polystyrenes, including styrene-containing polymers such as acrylonitrile-styrene copolymers, styrene-butadiene copolymers and styrene-vinylbenzylhalide copolymers; polycarbonates; cellulosic polymers, such as cellulose acetate, cellulose acetate-butyrate, cellulose propionate, ethyl cellulose, methyl cellulose, nitrocellulose, etc.; polyamides and polyimides, including aryl polyamides and aryl polyimides; polyethers; polyarylene oxides, such as polyphenylene oxide and polyxylylene oxide; polyesteramide-diisocyanates; polyurethanes; polyesters, including polyacrylates, such as polyethylene terephthalate, polyalkyl methacrylates, polyalkyl acrylates, polyphenylene terephthalate, etc.; polysulfides; polymers from monomers having alpha-olefinic unsaturation other than mentioned above such polyethylene, polypropylene, polybutene-1, poly-4-methylpentene-1, polyvinyls, e.g. polyvinylchloride, polyvinylfluoride, polyvinylidene chloride, polyvinylidene fluoride, polyvinyl alcohol, polyvinyl esters such as polyvinyl acetate and polyvinyl propionate, polyvinyl pyridines, polyvinyl pyrrolidones, polyvinyl ethers, polyvinyl ketones, polyvinyl aldehydes such as polyvinyl formal and polyvinyl butyral, polyvinyl amides, polyvinyl amines, polyvinyl urethanes, polyvinyl ureas, polyvinyl phosphates and polyvinyl sulfates; polyallyls; polytriazoles; polybenzobenzimidazoles; polycarbodiimides; polyphosphazines; etc., and interpolymers including block interpolymers containing repeating units from the above such as terpolymers of acrylonitrile-vinyl bromide-sodium salt of para-sulfophenylmethallyl ether; and grafts and blends containing any of the foregoing. Typical substituents providing substituted polymers include halogens such as fluorine, chlorine and bromine; hydroxyl groups; lower alkyl groups; lower alkoxy groups; monocyclic aryl; lower acyl groups and the like.

Brief Summary Text (31):

The hollow fiber membrane material is preferably as thin as possible in order to improve the rate of permeation through the membrane, yet of sufficient thickness to insure adequate strength to the hollow fiber membrane to withstand the separation conditions, including the differential pressures and differential partial pressures employed. Hollow fibers membranes may be isotropic, i.e. have substantially the same density throughout, or they may be anisotropic, i.e. having at least one zone

of greater density than at least one other zone of the fiber membrane. The hollow fiber membrane may be chemically homogenous, i.e. constructed of the same material, or it may be a composite membrane. Suitable composite membranes may comprise a thin layer which effects the separation on a porous physical support which provides the necessary strength to the hollow fiber membrane to withstand the separation conditions. Other suitable composite hollow fiber membranes are the multicomponent hollow fiber membranes disclosed by Henis et al in Belgian Pat. No. 860,811, published May 16, 1978 and herein incorporated by reference. These membranes comprise a porous separation membrane which substantially effects the separation and a coating material in occluding contact with the porous separation membrane. These multicomponent membranes are particularly attractive for gas separations including those for separating hydrogen and carbon dioxide from methane, carbon monoxide, nitrogen and other inert gases, in that good selectivity of separation and high flux through the membrane can be obtained.

Brief Summary Text (32):

The materials for the coating of these multicomponent membranes may be natural or synthetic substances, and are often polymers, which advantageously exhibit the appropriate properties to provide occluding contact with the porous separation membrane. Synthetic substances include both addition and condensation polymers. Typical of the useful materials which can comprise the coating are polymers which can be substituted or unsubstituted, and which are solid or liquid under gas separation conditions, and include synthetic rubbers; natural rubbers; relatively high molecular weight and/or high boiling liquids; organic prepolymers; polysiloxanes, silicone polymers; polysilazanes; polyurethanes; polyepichlorhydrins; polyamines; polyimines; polyamides including polylactams; acrylonitrile-containing copolymers such as poly (.alpha.-chloroacrylonitrile) copolymers; polyesters including polyacrylates, e.g. polyalkylacrylates and polyalkyl methacrylates wherein the alkyl groups have from 1 to about 8 carbon atoms, polysebacates, polysuccinates, and alkyd resins; terpinoid resins; linseed oil; cellulosic polymers; polysulfones, especially aliphatic-containing polysulfones; polyalkylene glycols such as polyethylene glycol, polypropylene glycol, etc.; polyalkylene polysulfates; polypyrrolidones; polymers from monomers having .alpha.-olefinic unsaturation such as polyolefins, e.g. polyethylene, polypropylene, polybutadiene, poly(2,3-dichlorobutadiene), polyisoprene, polychloroprene, polystyrene including polystyrene copolymers, e.g., styrene-butadiene copolymers, polyvinyls such as polyvinyl-alcohols, polyvinyl aldehydes, e.g. polyvinyl formal and polyvinyl butyral, polyvinyl ketones, e.g. polymethylvinylketone, polyvinyl esters, e.g. polyvinyl benzoate, polyvinyl halides, e.g. polyvinyl bromide, polyvinylidene halides, polyvinylidene carbonate, poly(N-vinylmaleamide), etc., poly(1,5-cyclooctadiene), poly(methylisopropenylketone), fluorinated ethylene copolymers, polyarylene oxides, e.g. polyxylylene oxide; polycarbonates; polyphosphates, e.g. polyethylenemethyl phosphate; and the like, and any interpolymers including block interpolymers containing repeating units from the above and grafts and blends containing any of the foregoing. The polymers may or may not be polymerized after application to the porous separation membrane.

Brief Summary Text (33):

In the present process the desired recovered methanol synthesis gas mixture comprising those gases permeated through the hollow fiber membranes is withdrawn from the bore of such membranes. The gas mixture has a much enhanced proportion of hydrogen and a substantial proportion of the carbon dioxide present in the purge gas stream removed from the recycled uncondensed reaction gas stream with substantially all of the methane and inert gases excluded therefrom. The permeated recovered gas mixture has been found to possess a relatively consistent composition of more than 85 mole percent hydrogen despite relatively wide variations in the mole percentages of the specific gases comprising the purge gas streams. It has also been found that despite a wide variation in the mole percentages of methane contained in such purge gas streams approximately 90 and often 95% of the methane

and inert gases are rejected by the membranes and excluded from permeated recovered synthesis gas mixtures.

Brief Summary Text (35):

The differential in pressure maintained between the purge gas stream contacting the outside of the hollow fiber membranes and the permeate stream within the bores of such membranes is a major variable involved in the present process, since it has been found to normally effect the volume percent of hydrogen and carbon dioxide present in the purge gas stream which can be recovered in the permeated gas product. Thus it has been found that the pressure differential may range from as low as about 3 to as high as about 100 atmospheres, depending upon the inherent strength and resistance to rupture of the hollow fiber membranes employed.

Preferably such differential will range from about 5 to about 50 atmospheres, and most typically from about 6 to about 40 atmospheres. The pressure of the purge gas stream contacting the shell side of the hollow fiber membranes can range from as low as 5 to about 100 atmospheres, and preferably ranges from about 5 to about 60 atmospheres and more preferably from about 7 to about 50 atmospheres. In contrast the pressure on the permeate gas stream in the bores of the hollow fiber membranes can range from as low as 1 to 95 atmospheres, preferably from about 5 to 55 atmospheres and typically from about 10 to about 30 atmospheres.

Brief Summary Text (36):

The permeated recovered methanol synthesis gas stream produced by the membrane separator treatment of the purge gas stream has been found to be suitable and advantageous for recycle to the methanol synthesis gas stream contacting the synthesis catalyst. Since the treatment of the purge gas stream by permeation of a portion thereof through the hollow fiber membranes has induced a pressure drop such permeated gas stream would require recompression before it could be combined with the recycle of the remaining uncondensed reaction gases for makeup with fresh synthesis gas and recontact with the methanol synthesis catalyst. In order to minimize the cost of compression it has been found advantageous to maintain a sufficient pressure upon the gas stream in the bores of membrane such that the permeated recovered gas stream can be combined with a stream of fresh synthesis gas mixture during its compression cycle. Thus, it has been found advantageous to maintain the pressure on the permeated recovered synthesis gas stream at approximately the pressure existing in the fresh synthesis gas stream between two stages of compression thereof. For example, if the fresh methanol synthesis gas is compressed in a first stage to about 25 atmospheres and in a second stage to about 45 atmospheres the permeated recovered gas stream can be conveniently combined with the fresh synthesis gas stream between the two stages of compression if the permeated gas stream is maintained at a pressure of about 25 atmospheres. The maintenance of such a pressure which still provides for a sufficiently large pressure drop for the recovery of the desired amounts of hydrogen and carbon dioxide has been found to be practical and desirable.

Brief Summary Text (38):

There is simultaneously produced a permeant or shell effluent gas stream from the outside of the hollow fiber membranes comprising the remainder of the gases present in the purge gas stream and of a relatively higher methane and inert gas content. Generally this methane rich permeant stream will comprise at least 50% hydrogen and contain approximately 90 or more percent of the methane and inert gases present in the initial purge gas stream. This methane rich permeant gas stream is suitable for any desired use in a particular installation. In many instances its optimum use may be as supplemental fuel gas to the furnace of the stream reforming unit commonly associated with methanol synthesis. In other instances it may find its optimum use when combined with the initial natural gas or hydrocarbon feed to the stream reformer for the recovery of the methane, carbon monoxide and carbon dioxide values present therein.

Brief Summary Text (39):

Control of the differential pressures between the purge gas stream contacting the outside of the hollow fiber membranes and the permeated recovered synthesis gas stream withdrawn from the bores of such membranes may be achieved by any convenient method. One suitable method of such control involves adjusting the pressures maintained by the pressure control valves in the respective streams. Total flows of the respective streams can also be controlled by means of flow control valves. In order to minimize recompression and the expense thereof one very suitable method to control such differential pressures will involve establishing a minimum pressure required in the permeated recovered synthesis gas stream for its recombination at a suitable point with the fresh methanol synthesis gas stream and varying by means of a pressure controller from a pressure just sufficient to establish permeation across the membrane up to the pressure at which the purge gas stream is separated from the uncondensed reaction gas mixture. In a typical low pressure methanol synthesis such pressures may typically comprise 25 atmospheres for the permeated recovered gas stream and range from about 27 atmospheres up to about 50 atmospheres, the pressure of the purge gas stream as it is separated in such typical process. During operation of the process if total flow of synthesis gas is for some reason diminished, adjustment can be made by restricting the flow of the permeant shell effluent gas stream and, consequently, the flow of the permeated recovered gas stream, or by varying the total surface area of membranes contacted by cutting out one or more parallel membrane separator vessels without the necessity of changing the pressures imposed on each stream or the pressure differential between them. Other suitable means of control which can be employed if desired, include control to a specific content of one or other of the desired gases as determined by analysis of such gases and effected by varying pressure differentials, flow rates and/or total membrane surface areas.

Detailed Description Text (2):

In this example and in Examples II and III which follow, methanol synthesis purge gas streams of varied composition drawn from an operating low pressure methanol synthesis process were treated in a separator vessel containing hollow fiber membranes. The separator vessel contained poly(siloxane)-coated anisotropic polysulfone hollow fiber membranes prepared substantially in accordance with the method disclosed in Example 64 of Belgian Patent 660,811 issued May 16, 1978 Henis et al. The polysulfone had a molecular weight in excess of 10,000 and the poly (siloxane) a molecular weight in excess of 1000 prior to crosslinking same. The hollow fiber membranes coated on the outer surface with poly(siloxane) had an inside diameter of 250 microns, an outside diameter of 500 microns, and a wall thickness of 125 microns. The hollow fiber membranes in the separator vessel had an effective surface area of 21.6 cm.². Purge gas samples were taken by direct sample tap of the recycle line of the uncondensed reaction gas mixture of an operating low pressure methanol synthesis process. Any condensate present was drained from the sample line and the gas sample allowed to flow to a gas cylinder via a high pressure coupling. After the gas pressures in the cylinder and the recycle synthesis gas line had equalized the gas cylinder was disconnected and employed to supply a sample of purge gas to the membrane separator.

Detailed Description Text (3):

Each cylinder of sample purge gas was individually analyzed by means of a gas chromatograph. Because of the pressure drop from the sample cylinder to the membrane separator. The water and methanol vapor content of the purge gas samples were well below saturation and the content of these vapors in the various purge gas samples were not determined. Pressures of the purge gas stream and of the permeant or effluent and permeate or recovered synthesis gas streams were constantly controlled. Compositions of both the permeant and permeate gas streams were determined by gas chromatographed analysis taken on continuous flow samples piped from the hollow fiber membrane module and in which at least three consecutive samples were identical in composition indicating steady state operation over an average of a 30 minute time span. Recorded analyses were determined by attaching an evacuated gas collecting bomb to the sample gas line. The gas in the filled bomb

was analyzed by gas chromatograph equipped with an integrator and computerized readout of the final results.

Detailed Description Text (5):

The above membrane separation unit was operated in co-current axial flow for a total period of over 950 hours of operation. It was operated at a temperature of 39.degree.-42.degree. C. to approximate the normal operating temperature in the synthesis gas recycle and purge gas lines of the operating plant.

Detailed Description Text (6):

The results of operating the membrane separator under varied pressure differentials, expressed as .DELTA.P in atmospheres, are set out in Table 1 below.

Detailed Description Text (7):

It will be observed that only modest changes in the composition of the permeate stream occur even though the differential pressures across the hollow fiber membranes were varied from 6.8 to 26.9 atmospheres (100 to 395 psi) .

Detailed Description Text (9):

The same membrane separation unit was operated in the same manner as set out in Example I at frequent intervals over an extended period utilizing cylinders of methanol synthesis process purge gas of varied composition. The reported samples of purge gas were taken respectively after 145, 439 and 951 hours of operation of the same membrane separator. In all instances the pressure differential was maintained at 6.8 atmospheres (100 psig) with a pressure of 1 atmosphere on the permeate stream in the bores of the hollow fiber membrane. Temperature in each of the runs was maintained at 40.degree.-41.degree. C. The composition of the varied purge gas streams subjected to treatment and of the permeate streams derived from each, expressed as mole percent of each constituent gas, is set out in Table 2 below.

Detailed Description Text (12):

The hollow fiber membrane separator is operated as described above using samples of purge gas withdrawn from an operating methanol synthesis plant for a total period of more than 950 hours. Gas chromatographic analyses of the purge gas streams and of the shell permeant and permeated recovered synthesis streams were conducted at intervals as required by any indicated change in process conditions as well as with every change of sample gas cylinders. For each such analysis of feed and product gases the intrinsic permeabilities (P/1) for the key component gases, hydrogen, carbon dioxide and methane, were determined. The intrinsic permeability or permeability coefficient of a membrane to a specific gas is determined by the relationship P/1 where P is the permeability defined as the cubic centimeters of gas passing through the membrane per square centimeter of surface area per second for a partial pressure drop of one centimeter of mercury per unit thickness, and 1 is the thickness of the membrane in centimeters. The intrinsic permeabilities or permeability coefficients for the key component gases of the hollow fiber membranes are found to be remarkably uniform with no signs of decline in such permeabilities after over 950 hours of operation. The results of the determination of intrinsic permeabilities P/1 are set out in Table 3 below.

Detailed Description Text (14):

The intrinsic permeabilities, P/1, of cellulose acetate hollow fiber membranes having an external diameter of 450 microns, an internal diameter of 250 microns and a wall thickness of 100 microns were determined for the principal component gases of a methanol synthesis process purge stream of the following composition:

Detailed Description Text (15):

The precent recovery of the hydrogen present and the percent rejection of the methane present in the purge gas stream were determined by computer simulation for treatment of 195 kg. mols/hr of this gas stream over two different total surface areas of the above cellulose acetate hollow fiber membranes, 1395 square meters and

2325 square meters. The results of such determination are set out in Table 4 below.

Detailed Description Text (17):

A methanol synthesis process operated at steady state with a total methanol synthesis gas throughput of approximately 6800 kg.-mols per hour and a purge gas stream of approximately 370 kg.-mols per hour removed from the recycling uncondensed reaction gas line and directed to fuel. The purge gas stream was thoroughly analyzed and its composition determined at steady state operation. The compositions of a permeated recovered synthesis gas stream and a permeant fuel gas stream were determined based upon computer calculations employing a membrane separation unit composed of identical hollow fiber membranes to those described in Example 1. The hollow fiber membranes comprise anisotropic polysulfone hollow fiber membranes, the polysulfone having a molecular weight in excess of 10,000, the outer surfaces coated with poly(siloxane), which has a molecular weight in excess of 1,000 prior to crosslinking to provide a silicone rubber, produced as described in Example 1. The hollow fiber membranes have the dimensions there described. The separation units contain the number of such hollow fiber membranes to provide a total surface area of approximately 5600 square meters.

Detailed Description Text (18):

In operation of the improved process for increased methanol recovery the volume of purge gas removed from the uncondensed reaction gas recycle line is increased to 493.5 kg.-mols per hour in order to provide for the removal of the same amount of methane as in the previous operation. The pressure of the purge gas stream is the same as the recycling uncondensed reaction gases and is maintained at 46.7 atmospheres. The purge gas stream is passed first to a demister unit, a packed column suitably sized for the removal of all liquids entrained with the purge gas stream. Thereafter the purge gas stream is passed directly to the shell of the hollow fiber membrane separation unit or units in parallel comprising a cylindrical shell containing one or more bundles of the above-described hollow fiber membranes suitably manifolded for the removal of the permeate gas stream from the bores thereof and with appropriate purge gas inlet and permeant outlet ports. In the membrane separation unit or units the purge gas stream is split into two portions consisting of shell effluent gas and permeated recovered synthesis gas streams.

Detailed Description Text (20):

The permeated recovered synthesis gas stream amounting to some 280 kg.-mol/hr is withdrawn from the bores of the hollow fiber membrane and manifold header and directed to the pressure stage of the fresh methanol synthesis gas operation. The pressure between the first and second stage of compression of the methanol synthesis gas at this point is approximately 25 atmospheres and the recovered synthesis gas can conveniently be combined therewith. The combined streams will thereafter be subjected to compression and circulation to the methanol synthesis catalyst in the usual manner. The permeant or shell effluent gas stream comprising about 213 kg.-mol/hr is directed to a fuel gas header for eventual use as burner fuel for the stream reforming process. It will be observed from Table 5 that the increase in volume of purge gas removed from the recycling reaction gas line is sufficient to provide for the same amount of methane rejected from the recycled recovered synthesis gas and directed to fuel as in the prior process. Therefore the purge rate of the methane and other inert gases is maintained in balance in the total circulating methanol synthesis gas system.

Detailed Description Text (22):

In an alternative to the above process the purge gas stream after removal from the recycling uncondensed reaction gas stream is directed to a packed column water scrubber which absorbs from the purge gas stream 95% of the methanol present as vapor in the purge gas stream. The water and methanol solution from the scrubber is directed to the distillation column of an associated crude methanol purification unit where such absorbed methanol is recovered. The scrubbed purge gas is then

directed to a demister unit which removes any entrained water from the purge gas and thence to the membrane separation unit as described above. The resulting recovery of added methanol, amounting to some 49 kg.-mol/hr from increased methanol synthesis from the recovered hydrogen and carbon dioxide synthesis gas and methanol recovered in the water scrubber is set out in Table 6 below.

Detailed Description Paragraph Table (5):

Table 4 Cellulose Acetate Hollow Fiber
Membranes 1395m.sup.2 % 2325m.sup.2 % P/1 .times. 10.sup.-5 Recovery-Rejection
Recovery-Rejection H.sub.2 7.0 36.1 48.5
CH.sub.4 .15 93.8 89.0

CLAIMS:

1. In a methanol synthesis process wherein methanol is synthesized from a synthesis gas comprising hydrogen and carbon dioxide by passing said synthesis gas over a methanol synthesis catalyst at methanol-forming conditions to form a gaseous mixture including methanol, water and unreacted carbon dioxide, said gaseous mixture is cooled, methanol and water are condensed therefrom and separated from the uncondensed gaseous mixture, a portion of said uncondensed gaseous mixture is removed as purge gas and the remaining uncondensed gaseous mixture is recycled to contact said methanol synthesis catalyst, the improvement comprising contacting said purge gas with the outside surfaces of a plurality of hollow fiber membranes selectively permeable to both hydrogen and carbon dioxide to form a permeant gas stream depleted in hydrogen and carbon dioxide and a permeate gas stream enriched in both said gases, and combining said enriched permeate gas stream with said synthesis gas.

2. The process of claim 1 wherein said removed purge gas is treated to recover methanol vapor therein prior to contacting said purge gas with said membranes.

9. The process of claim 1 wherein said hollow fiber membranes have outside diameters of from about 150 to about 800 microns and a wall thickness of about 50 to about 300 microns.

10. The process of claim 1 wherein said membranes are multicomponent hollow fiber membranes which comprise a porous hollow fiber separation membrane and a coating in occluding contact with the outside surface thereof.

11. The process of claim 10 wherein said separation membrane comprises polysulfone and said coating comprises poly(siloxane).

12. In a methanol synthesis process wherein methanol is synthesized from a synthesis gas comprising hydrogen and carbon dioxide by passing said synthesis gas over a methanol synthesis catalyst at methanol-forming conditions to form a gaseous mixture including methanol, water and unreacted carbon dioxide, said gaseous mixture is cooled, methanol and water are condensed therefrom and separated from the uncondensed gaseous mixture, a portion of said uncondensed gaseous mixture is removed as purge gas and the remaining uncondensed gaseous mixture is recycled to contact said methanol synthesis catalyst, the improvement comprising contacting said purge gas with the outside surfaces of a plurality of hollow fiber membranes selectively permeable to both hydrogen and carbon dioxide and having an outside diameter of from about 150 to 800 microns and a wall thickness of from about 50 to 300 microns to form a permeant gas stream depleted in hydrogen and carbon dioxide and a permeate gas stream enriched in both said gases, and combining said enriched permeate gas stream with said synthesis gas.

13. The process of claim 12 wherein said removed purge gas is treated to recover methanol vapor therein prior to contacting said purge gas with said membranes.

20. The process of claim 12 wherein said membranes are multicomponent hollow fiber membranes which comprise a porous hollow fiber separation membrane and a coating in occluding contact with the outside surface thereof.

21. The process of claim 20 wherein said porous separation membrane comprises polysulfone and said coating comprises poly(siloxane).

22. The process of claim 20 wherein said porous separation membrane comprises polysulfone having a molecular weight of at least about 10,000 and said coating comprises poly(siloxane) cross-linked to provide a silicone rubber.

23. In a methanol synthesis process wherein methanol is synthesized from a synthesis gas comprising hydrogen and carbon dioxide by passing said synthesis gas over a methanol synthesis catalyst at methanol-forming conditions to form a gaseous mixture including methanol, water and unreacted carbon dioxide, said gaseous mixture is cooled, methanol and water are condensed therefrom and separated from the uncondensed gaseous mixture, a portion of said uncondensed gaseous mixture is removed as purge gas and the remaining uncondensed gaseous mixture is recycled to contact said methanol synthesis catalyst, the improvement comprising contacting said purge gas with the outside surfaces of a plurality of hollow fiber membranes selectively permeable to both hydrogen and carbon dioxide and having an outside diameter of from about 150 to 800 microns and a wall thickness of from about 50 to 300 microns to form a permeant gas stream depleted in hydrogen and carbon dioxide and a permeate gas stream enriched in both said gases, adding carbon dioxide gas to the enriched permeate gas stream, and combining said enriched permeate gas stream with said synthesis gas.

25. The process of claim 23 wherein said membranes are multicomponent hollow fiber membranes which comprise a porous hollow fiber separation membrane and a coating in occluding contact with the outside surface thereof.

26. The process of claim 25 wherein said porous separation membrane comprises polysulfone and said coating comprises poly(siloxane) cross-linked to provide a silicone rubber.

30. The process of claim 23 wherein methanol vapor in said purge gas is absorbed in a water scrub prior to contacting said purge gas with said membranes.

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L4: Entry 4 of 256

File: USPT

Jul 5, 2005

DOCUMENT-IDENTIFIER: US 6914169 B1

TITLE: Patch agent

Brief Summary Text (5):

Therefore, research and development have been under way from the viewpoint of the elasticity of support, the adhesiveness of adhesive layer, and the like in order to satisfy both high peeling prevention (resistance to peel) and low skin irritation (suppression of rashes in the skin and pains upon peeling), and various patch agents have been proposed. For example, Japanese Patent Application Laid-Open No. HEI 9-255563 discloses a technique in which the ratio in length between the longer and shorter sides in a rectangular patch agent and the bending resistance in the longitudinal direction are controlled so as to yield a skin traceability. Also, Japanese Patent Application Laid-Open No. HEI 10-226638 discloses a technique in which a support having a low bending resistance is provided with an adhesive planar substance, so as to provide the support with a softness. Further, Japanese Patent Application Laid-Open No. HEI 11-35453 discloses a patch agent whose adhesive layer contains oleic acid alkyl ester, so as to reduce the peeling force.

Detailed Description Text (13):

When necessary, compounding agents such as tackifiers, softeners, fillers, age resistors, and absorption accelerators may be added to the adhesive layer used in the present invention. Examples of such compounding agents include tackifiers such as alicyclic saturated hydrocarbon resins (manufactured by Arakawa Chemical Industries, Ltd. under the trade names of Alcon P-100 and the like), hydrogenated rosin esters (manufactured by Arakawa Chemical Industries, Ltd. under the trade names of KE-311 and KE-100, and manufactured by Hercules Incorporated under the trade names of Foral 105, Foral 85, and the like), hydrogenated alicyclic hydrocarbons (manufactured by Exxon Chemical Co. under the trade names of Escorez 5300 and the like), polyterpene resins, petroleum resins, and phenol resins; softeners such as liquid paraffin, polybutene, liquid polyisobutylene, and animal and vegetable oils; other fillers; age resistors; and the like. Also, when necessary, absorption accelerators may be added to the above-mentioned pressure-sensitive adhesive in order to improve the skin permeability of medicine. Examples of such absorption accelerators include isopropyl myristate, diethyl sebacate, sorbitan monolaurate, sodium oleylphosphate, sodium laurylsulfate, octylphenyl ethers, lauryl ethers, sorbitan monolaurate, lauroyl diethanolamide, lauroyl sarcosine, oleoyl sarcosine sugar esters, lecithin, glycyrrhizin, urea, salicylic acid, calcium thioglycolate, lactic acid, lactic acid esters, olive oil, squalene, lanolin, liquid paraffin, glycerin, and the like. Further, when necessary, pigments, flavors, UV-absorbents, surfactants, pH-adjusters, and the like may appropriately be compounded in the above-mentioned pressure-sensitive adhesive.

Detailed Description Text (15):

As the thickeners used in the moisture-containing ointment in accordance with the present invention, those which can stably hold a moisture of 30% to 80% and have a water retention are preferable. Preferably employable as specific examples thereof are water-soluble polymers such as natural polymers including those of vegetable type such as guar gum, locust bean gum, carrageenan, alginic acid, sodium alginate, agar, gum arabic, tragacanth gum, karaya gum, pectin, and starch, microorganic type such as xanthan gum and acacia gum, and animal type such as gelatin and collagen;

semi-synthetic polymers including those of cellulose type such as methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, and sodium carboxymethyl cellulose, and starch type such as soluble starch, carboxymethyl starch, and dialdehyde starch; and synthetic polymers including those of vinyl type such as polyvinyl alcohol, polyvinyl pyrrolidone, and polyvinyl methacrylate, acrylic type such as polyacrylic acid and sodium polyacrylate, and other synthetic polymers such as polyethylene oxide and methyl vinyl ether/maleic anhydride copolymer.

Detailed Description Text (16):

In particular, as such a thickener, polyacrylic acid is preferable in that it has a high gel strength and is excellent in water retention, and sodium polyacrylate having an average degree of polymerization of 20000 to 70000 is more preferable. As the average degree of polymerization becomes lower than 20000, the thickening effect tends to decrease, so that a sufficient gel strength may not be obtained. As the average degree of polymerization becomes higher than 70000, on the other hand, the thickening effect tends to become so strong that the operability may lower.

Detailed Description Text (18):

Also, propylene carbonate, crotamiton, L-menthol, mentha oil, limonene, diisopropyl adipate, and the like as a solubilizer or absorption accelerator; and methyl salicylate, glycol salicylate, L-menthol, thymol, mentha oil, limonene, nonylic acid vanillylamine, pepper extract, and the like as an efficacy adjuvant may be added to the moisture-containing ointment in accordance with the present invention. Further, when necessary, stabilizers, antioxidants, emulsifiers, and the like may be added to the moisture-containing ointment in accordance with the present invention.

Detailed Description Text (19):

Further, when necessary, crosslinking agents, polymerizers, and the like may be added to the moisture-containing ointment so as to strengthen the moisture-containing ointment (adhesive) and cause it to yield water retention. Such crosslinking agents and polymerizers can appropriately be chosen according to the kind of thickeners and the like.

Detailed Description Text (20):

For example, in the case where polyacrylic acid or polyacrylate is employed as a thickener, compounds having at least two pieces of epoxy group in a molecule; inorganic acid salts such as hydrochlorides, sulfates, phosphates, and carbonates of Ca, Mg, Al, and the like; organic acid salts such as citrates, tartrates, gluconates, and stearates; oxides such as zinc oxide and silicic anhydride; and polyvalent metal compounds such as hydroxides like aluminum hydroxide and magnesium hydroxide are preferably used. In the case where polyvinyl alcohol is employed as a thickener, adipic acid, thioglycolic acid, epoxy compounds (epichlorohydrin), aldehydes, N-methylol compounds, and complexes of Al, Ti, Zr, Sn, V, Cu, B, and Cr are preferably used. When polypyrrolidone is employed as a thickener, methyl vinyl ester/maleic anhydride copolymer, polyacid compounds, or alkali metal salts (polyacrylic acid, tannic acid, and their derivatives) are preferably used. When polyethylene oxide is employed as a thickener, peroxide or polysulfone azide is preferably used. When methyl vinyl ether/maleic anhydride copolymer is employed as a thickener, polyfunctional hydroxyl compounds, polyamines, iodine, gelatin, polyvinyl pyrrolidone, iron, mercury, and lead salts are preferably used. When gelatin is employed as a thickener, aldehydes such as formaldehyde, glutaraldehyde, dialdehyde starch; diepoxides such as glyoxal and butadiene oxide; diketones such as divinyl ketone; and diisocyanates are preferably used.

Detailed Description Text (37):

Into a mixer, 31.92 parts by weight of purified water, 3 parts by weight of gelatin, 3 parts by weight of polyvinyl pyrrolidone, and 3 parts by weight of zinc oxide were introduced; and they were mixed at a temperature of about 50.degree. C., whereby a uniform dispersion was obtained. Then, a dispersion prepared beforehand

comprising 50 parts by weight of polyethylene glycol, 4 parts by weight of sodium polyacrylate, 3 parts by weight of polyacrylic acid, and 0.08 parts by weight of polyethylene glycol diglycidyl ether were added to the former dispersion, and stirred and mixed therewith. Further, a solution in which 0.5 part by weight of suprofen was dissolved into 1.5 parts by weight of benzyl alcohol was added thereto and stirred and mixed therewith, whereby a uniform mixture was obtained.

Detailed Description Text (52):

Into a reactor, 55 parts by weight of acrylic acid 2-ethylhexyl ester, 26 parts by weight of acrylic acid methoxyethyl ester, 14.7 parts by weight of vinyl acetate, 0.3 part by weight of azobisisobutyronitrile, and 100 parts by weight of ethyl acetate were introduced. Subsequently, they were heated to 60.degree. C. in a nitrogen atmosphere so as to initiate polymerization, the reaction was carried out for 10 hours, and then the mixture was further matured for 2 hours at 60.degree. C., whereby a copolymer solution was obtained. To thus obtained copolymer solution, 4 parts by weight of ketoprofen were added; and they were mixed together, whereby a uniform mixture solution was obtained.

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